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ACIDIC PRECIPITATION IN ONTARIO STUDY

AN ASSESSMENT OF THE PERFORMANCE OF THE CUMULATIVE PRECIPITATION MONITORING NETWORK, JUNE 1980 - DECEMBER 1981

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1.0 INTRODUCTION

This report evaluates the network performance based on data reported from the APIOS (Acidic Precipitation in Ontario Study) cumulative precipitation monitoring network during the period from June 1980 to December 1981. A data listings report entitled "Monthly/28 Day Cumulative Precipitation Chemistry Listings, June 1980 - December 1981" has previously been published (1).

The cumulative precipitation network utilizes MIC Type "A" wet-only precipitation collectors colocated with precipitation storage gauges which act as the primary standards of the precipitation depth. Precipitation samples are collected over monthly periods in new polyethylene bags inserted into the buckets of the collectors. Operators collect precipitation samples and technicians visit the sites after every sampling period to pick up the samples as well as to check and maintain the instrumentation. The detailed technical and operating procedures which are used in the cumulative precipitation network are contained in a separate document (2).

This performance evaluation primarily consists of utilizing field and office observations, and validation flags which are appended to the published data. Laboratory performance is presented by using available laboratory quality control (QC) data obtained during the 1980 sampling periods.

Quality assurance (QA) reports will be published in the future on an annual basis. These reports will be more comprehensive and will contain the results of QA activities that have been implemented since 1981. Quality assurance has been recognized to be of utmost importance to the success of the APIOS monitoring program. A QA plan has been developed and implemented to ensure that data reported in the monitoring network are accurate, precise, complete, and representative (3).

Contained in Table 1 are the monitoring site names and corresponding numbers which have been used in this report. Table 2 provides a listing of the monitoring regions within the Province and the corresponding sites within each region. A site map of the cumulative network is presented in Figure 1.

2.0 FIELD OBSERVATIONS

Field observations are appended to the data as codes to indicate sampling problems and the conditions of samples prior to analyses. These observations include foreign matter (insects, leaves, particulates, or fibres) collected in the samples, sample leaks, spills, or sampler malfunctions during the collection periods. The following sections describe these observations as they pertain to the 1980-81 cumulative precipitation data.

2.1 Sampler Malfunctions

Sampler malfunction coding for this evaluation includes sampler malfunctions, hydro failures, missed events, or any other conditions that may have affected a sample during the collection period. Therefore, any sample which was coded either as events missed (coded I), wet side open when not precipitating (coded J), no precipitation collected (coded K), part of event missed (coded L), or sampler malfunctioned (coded F), in the data report (1) was considered as a sampler malfunction in this evaluation.

Combining all data, 22.7% of all samples collected reported a sampler malfunction (a total of 503 samples were collected from 34 monitoring sites). The percentage of sampler malfunctions for individual sites is shown in Figure 2. The percentage of sampler malfunctions on a regional basis is shown in Figure 2b. Average sampler malfunction frequencies in the regions ranged from 15.3 (Northeastern) to 39.1 (Northwestern) percent. Close to 70% of all sites in the network experienced less than 25% sampler malfunctions. A histogram of sampler malfunctions is shown in Figure 3. Six sites (Shallow Lake, Coldwater, Dorset, Moonbeam, Ear Falls, and Pickle Lake) recorded 40% or greater sampler malfunctions. Since the network only began operating during the fall of 1980, it can be expected that sampler malfunctions would decrease as new personnel gained experience maintaining the sampling equipment and because of improvements in instrumentation design.

Figure 4 presents a graph of sampler malfunctions versus sampling months for 1981. Unexpectedly, the month of June recorded the highest percentage of sampler malfunctions. Because of the severe weather and operating conditions during the winter sampling months, it was expected that the highest malfunction percentages would occur during December to March. If the month of June is omitted, higher malfunctions did prevail during December, January, and February. However, no explanation is known for the high number of sampler malfunctions that occurred in June.

Operator and field submission sheets were scanned to determine the most common sources of malfunctions. Only 59 out of a possible 114 malfunctions were described on these sheets in terms of the type of malfunction which occurred. Of these 59 malfunctions, there were 20 blown fuses, 13 hydro failures, 10 ground fault interruptions, 9 printed circuit board failures, 4 limit switch failures, and 3 slipping clutches or sprockets.

Blown fuses, while accounting for one half of all reported malfunctions, are only symptoms of other underlying causes. Moisture within the collector housing, incorrectly adjusted limit switches, failed limit switches, poor electrical connections, or defective printed circuit boards are all conditions which can blow fuses within the sampler.

2.2 Sample Leaks or Spills

Whenever a sample has leaked or been spilled, the code G (or H) is appended to the sample in the data report. The leak/spill code is always appended regardless of the amount of sample lost.

Leaks primarily occur during 1) the freezing and thawing cycles which occur during the sampling period or 2) handling and transport from the time of collection to final analyses. Sample spills occur infrequently in the cumulative network, but may occur if a sample is dropped or mishandled during the bag sealing procedure.

During 1980-81, 20.7% of all samples leaked. As indicated in Figure 5 the majority of leaks (almost 70%) occurred during the months from September to February. December accounted for more than 22% of all leaks.

The sampling bags used during 1980-81 were constructed of polyethylene. A different type of bag was introduced in the beginning of 1983 to reduce the number of leaks. These new bags are made of polyethylene with nylon laminated on the outside of the polyethylene. Preliminary results and observations indicate that this new type of bag has decreased the frequency of leaks experienced in the past.

Figures 6 and 7 show the percentage of leaks and spills for each site and region. The Northeastern and Southeastern regions have considerably higher percentages of leaks compared to other regions. Approximately 30% of all samples submitted from these two regions leaked. The remaining regions have, on average, 14% sample leaks. At this time, no explanation can account for these differences.

2.3 Samples Lost or Not Submitted

Samples that are not submitted for chemical analyses (coded E) may be due to a number of circumstances. Sampler malfunctions or sample leaks may

result in samples not submitted for analyses (i.e. no sample volume collected). Overall, 5.4% of all samples in the network were lost (coded X) or not submitted for analyses (2.2% lost, 3.2% not submitted). Figure 8 presents the percentages of samples lost or not submitted for analyses on a regional basis.

The Northwestern region sites have more than twice the combined percentage from all other regions of lost and not submitted samples (11.6% were not submitted or lost from NW). In particular, 8.7% of all samples from the Northwestern Region were not submitted for analyses. The majority of these samples not submitted for analyses were due to instrument malfunctions. Since a dedicated technician was not available at the onset of the sampling program, a lack of manpower accounted for some of these instrument problems within this region. As well, the newly designated APIOS technician was relatively inexperienced during the first few months of this period.

As earlier stated, 2.2% of all samples were lost (11 out of 503 samples). Of these 11 lost samples, 10 samples were lost from October to December, 1980. It is unknown whether these losses were due to courier problems or samples being misplaced in the laboratory.

2.4 Samples Unaffected

Samples which have not been coded as having sampler malfunctions (codes F, I, J, K, L), or coded as lost or not submitted samples (codes X, E) are considered "unaffected" samples for the following observations.

Presented in Figure 9 are the percentage of unaffected samples for each monitoring site. Over 80% of all sites had 60% or greater unaffected samples. Sites experiencing problems (< 60% unaffected) were Dorset (9 of 19 samples), Moonbeam (7 of 16 samples), Pickle Lake (7 of 17 samples), and Ear Falls (12 of 16 samples). Huron Park (2 of 3 samples), and Coldwater (2 of 4 samples), while having less than 60% unaffected samples, were installed late in 1981 and therefore the observation cannot be considered representative because of the small number of collected samples.

Looking in detail at the sites having a high percentage of affected samples, some general comments can be made with respect to isolating the reasons for these higher percentages. Instrumentation problems and the trouble-shooting of these problems are crucial in obtaining good data recovery. For some of these sites, a precipitation sampler would malfunction consistently over consecutive months. Many times the exact cause of the malfunction may not have been known during a technician visit. By replacing a component such as a fuse or by adjusting a

switch, the sampler would begin to operate properly again even though the source of the malfunction had still not been corrected for. This can occur with sticky limit switches, incorrect switch adjustments, or "problem" printed circuit boards.

Besides sampler breakdowns, hydro failures and circuit breakers were a problem at some sites. Sites experiencing circuit breaker problems have been modified so that the ground fault interrupter is located near or in the receptacle and not near the service panel.

2.5 Data Recovery

During the 1980-81 sampling period, 34 monitoring sites became operational. Data recovery for this period has been calculated by dividing the total number of reported data points by the expected number of data points. For every precipitation sample there should be 24 data points (complete analyses including metals). Therefore, it is expected that for any given site, the expected number of data points is 24 multiplied by the number of operating periods. Data recovery is therefore a reflection of instrumentation, sample handling, or any other sampling protocol that could affect the completeness of the data set. Unreliable data due to "siting" problems or any other form of contamination is still considered recoverable data in this section.

Presented in Figure 10 is the percentage of recovered data for all monitoring sites. The overall data recovery average of the network during 1980-81 was 83.4%. Five sites incurred data recovery percentages below 75%. These sites were McKellar (72.1%), Moonbeam (72.7%), Attawapiskat (61.7%), Ear Falls (57.8%), and Pickle Lake (63.7%). For all of these sites except Attawapiskat, sample leaks and sampler malfunctions were significant in affecting good data recovery. Attawapiskat was affected by leaks, malfunctions, or lost samples in only 13% of all samples but still experienced a low data recovery. This is due primarily to smaller precipitation amounts, and therefore the lack of adequate sample volume for complete chemical analyses.

Shown in Figure 11 is a histogram of data recoveries. The majority of monitoring sites fell in a group with 81 to 95 percent data recovery. It is interesting to note that while some sites experienced a high percentage of sampler malfunctions, these same sites had very good data recoveries. One example of this is the Dorset site. From Figure 2, Dorset incurred sampler malfunctions in 47.4% of all samples. However, data recovery for this site was 93.6%. Since the technician is located on site, any sampler malfunction was quickly detected and repaired. Also, upon closer inspection of the reasons for these sampler malfunc-

tions in Dorset, blown fuses were significant (5 out of 9 malfunctions). Many of these malfunctions did not affect the samples (i.e. no events missed) and sampling continued uninterrupted. Therefore, the frequency of sampler malfunctions may not truly reflect whether data recovery has been good or bad in some cases. All technicians are presently instructed to code a sampler malfunction only if the malfunction has affected the integrity or representativeness of the sample.

3.0 DATA VALIDATION OBSERVATIONS

Data validation consists of using various screening techniques, checks, and statistical routines which are applied to identify unusual or suspect data. During these procedures office comment codes and validation flags may be appended to individual analytical results. For details of these procedures, consult the "APIOS Technical and Operating Manual" (2). These office comment codes and flags have been evaluated and are presented below for the 1980-81 cumulative precipitation data.

3.1. Sampler Efficiencies

Sampler efficiencies are calculated by converting the sample volume to an equivalent precipitation depth and comparing this converted depth to the precipitation storage guage depth. Any efficiency less than 50% or greater than 120% is deemed abnormal and the comment code N is appended to the sample. If any sample had been coded as a sample leak, no sampler efficiency was reported, however, the code N was still appended to the sample.

The average sampling efficiency of all sites for the 1980-81 sampling period was 61.4%. The average efficiency from May to October was 71.3%, and from November to April, 53%. The average sampling efficiencies of all sites are shown in Figure 12.

During the 1980-81 sampling period, 31.6% (159 out of 503) of all sampler efficiencies were coded abnormal. Figure 13 shows the frequency of these abnormal efficiencies on a monthly basis for 1981. From this figure, abnormal efficiencies on average occur uniformly throughout the year. The number of abnormal efficiencies during 1980-81 is unexpectedly high (31.6%), therefore a portion of data (September 1980 to December 1981) was scrutinized to account for these abnormalities.

The total number of calculated efficiencies for this period was 488, and of these 132 were abnormal (27%). Of these 132 abnormal efficiencies, 89 can be accounted by coded spills or leaks, coded incorrect volumes, and sampler malfunc-

tions (see Figure 14). Therefore, 43 of the original 132 abnormal efficiencies could not be accounted for. This represents 8.8% (43 out of 488) of all sampler efficiencies which are coded abnormal and cannot be accounted for.

This observation indicates that using the storage gauge to calculate gauge depths is acceptable if proper procedures are adhered to. Extreme care must be taken when measuring and calculating gauge depths. If this care is taken and if sampler malfunctions are kept to a minimum, the sampler efficiencies would be expected to improve.

3.2 Calculated/Observed Discrepancies and Unreliable Results

Discrepancies between the calculated and observed conductance, pH, and ionic balance are appended to samples in the data report as codes "C", "H", and "M" respectively. Gross limit checks are applied and outliers are screened. Any results deemed unreliable after further manual screening are flagged by the code "U". Details of these validation procedures are described elsewhere (4).

The average percentage of conductivity discrepancies in the network was 8.8%; pH discrepancies 11.3%, and ionic balance discrepancies 4.6%. The network average of unreliable results was 5.3% (560 out of 10,472 results). Note that volumes coded as unreliable were not included in this estimate.

Table 3 provides the percentages of samples from every site which have been coded as a calculated/observed discrepancy or unreliable result. Seven sites have been singled out due to higher percentages of these discrepancies and unreliable results. These sites are Milton, Smith's Falls, Dalhousie Mills, Moonbeam, Attawapiskat, Nakina, and Pickle Lake.

The Milton monitoring site (site number 10) located less than 1 km from the major highway 401 had the largest percentage of unreliable data, namely 19.4%. Also, 26.7% of all samples were coded as having calculated/observed pH discrepancies; 60% of sample pH's were unreliable; 43% of calcium results were unreliable; 40% of the chloride results were unreliable; and 79% of the magnesium results were unreliable. Preliminary results of the 1982 data show the same trend. Comparing the Milton site data to those of the Waterloo site (50 km apart), significantly higher pH values are observed. Higher concentrations are observed in Milton for the soil related parameters, calcium and magnesium (see Table 4). Contamination from a soil related source is strongly suspected of the samples collected at Milton. For these reasons, the Milton monitoring site was removed from the network during the spring of 1984.

Smith's Falls (site number 15) had 8.8% unreliable results and 26.7% of all pH results were coded as discrepancies. Dalhousie Mills' (site number 16) data

on average were 10.5% unreliable with 12.5% discrepancies of conductivity values, pH values, and ionic balances. 7.4% of all results were coded unreliable for Moonbeam (site number 27) along with 12.5% of conductivities and 25% of pH values coded as discrepancies. A sampler malfunction occurred for every observed discrepancy for Moonbeam, therefore it cannot be ascertained whether the discrepancies were site or sampler related. These three sites should be scrutinized for site representativeness with the 1982 data. Based on a more complete data set, better judgements of the data quality at these sites can be made.

Attawapiskat (site number 28), Nakina (site number 30), and Pickle Lake (site number 36) consistently show discrepancies that may indicate contamination due to siting problems. Nakina has already been removed from the monitoring network due to the observation of persistent elevated pH values (46.7% of all pH's were coded as discrepancies) resulting from high concentrations of calcium, magnesium, and potassium.

Attawapiskat displays similar contamination problems to those of Nakina. Higher concentrations of calcium, magnesium, and elevated pH values indicate local soil-related contamination. Conductivity discrepancies occurred in 23.1% of all samples. 38.5% of all pH values were coded as discrepancies and 23.1% ionic balance discrepancies occurred. 11.5% of all data was flagged unreliable. The Attawapiskat site located on a native reservation is situated near the shore of James Bay. Nearby dirt and gravel roads (50 meters away) are probably a significant source of dry contamination. To add to this problem, vandalism has occurred on several occasions. For these reasons, Attawapiskat was removed from the monitoring network in 1983.

Pickle Lake had 9.1% unreliable data. Conductivity discrepancies occurred in 21.4% of all samples; 28.6% of all samples had pH discrepancies, and 14.3% ionic balance discrepancies in samples were identified. Data collected during 1982 from Pickle Lake may indicate similar problems. Possibly data collected by the CANSAP and CAPMoN samplers, which are located at the same site, may help substantiate any conclusions made regarding this site's representativeness.

Discrepancies (conductivity, pH, and ionic balance) on a regional basis are provided in Figure 15. The Northwestern region's percentages of samples with discrepancies are significantly higher than those of all other regions. This reflects the difficulties in finding representative sites in Northern Ontario.

The percentage of unreliable results on the basis of parameter type is shown in Table 5. pH values were the most frequent unreliable result (15.4% of all pH values). Calcium (10.4%), magnesium (10.5%), and sodium (7.7%) followed as parameters with the most frequent unreliable result codings.

4.0 LABORATORY QUALITY CONTROL DATA

All samples in the cumulative precipitation network during 1980-81 were analyzed at the Ministry of the Environment's laboratory located on Resources Road in Toronto. Two sections, namely the Water Quality (WQ) and Inorganic Trace Contaminants (ITC) Sections, carried out all sample analyses.

The following section will summarize the precision and accuracy of the Water Quality Section based on a minimum of three month's quality control data during 1980. Performance reports for all individual laboratory tests are attached in Appendix 1. Precision estimates are all based on one standard deviation.

Quality control data similar to the Water Quality Section's performance reports have also been made available from the ITC Section on metals analysis. Performance reports of these data are attached in Appendix 2.

4.1 Water Quality Parameters

Calibrations were carried out by using standardized solutions covering the range of instrument response. Calibrations are confirmed by using two quality control standards (QC-A and QC-B) which are made up and maintained independently of the calibration standards. The accuracy of laboratory measurements are represented by the percentage differences between the control standard concentrations and the mean concentrations obtained during calibrations.

Table 6 provides a list of water quality parameters and the associated accuracies using the control standards. To control both the blank and slope bias during calibration, the control concentrations of QC-A and QC-B are chosen to be approximately 70% and 10% of full scale respectively.

Precision in the Water Quality Section (within-run repeatability) is represented by the standard deviations of the differences observed between within-run duplicate analysis of routine samples. Table 7 lists all water quality parameters and the standard deviations of the differences of duplicate results. The observed differences in duplicate results were accumulated and sorted according to three concentration ranges, namely 0-20%, 20-50%, and 50-100% of full scale. A standard deviation was then calculated for each of these three concentration ranges. Only concentration ranges of 0-20% and 20-50% full scale are presented in Table 7 since the majority of sample results lie within these two ranges.

Table 8 summarizes the accuracy and precision of the Water Quality Section during the three month period in 1980. The accuracy of every water quality parameter is expressed as a $\pm$ percentage based upon Table 6 using the following expression:

$$\left| \frac{\text{Theoretical Conc. - Observed Conc.}}{\text{Theoretical Concentration}} \right| \times 100$$

The precision of every parameter is based upon Table 7 using the coefficient of variation:

$$\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

It should be noted that percentage differences of small concentrations may be misleading. For example, a percentage error of ± 30% using a concentration of 0.08 mg/l converts to an error of ± 0.02 which corresponds to an interval of 0.06 to 0.10. Therefore, the concentration level must always be kept in mind when interpreting accuracies and precision. Percentages have been introduced since future field QC data, where worse precision and accuracy estimates are expected, will be expressed as ± percentages.

All water quality parameters except for conductivity (±11%), had accuracies within ± 10%. Precision estimates varied with parameter type. Acid-base related parameters (total H^+, sulphate, nitrate) had precisions within ± 5%. All other parameters except potassium (±15%), sodium (±10%), and phosphorous (±12%) had precisions less than ± 10%.

4.2 Inorganic Trace Contaminants

The Inorganic Trace Contaminants Section (ITC) is responsible for the heavy metal analysis of cumulative precipitation samples. Aqueous samples with sufficient volume ($\geq$ 100 mls) are analysed by preconcentration followed by the Inductively Coupled Argon Plasma (ICP) method. For samples with limited volume ($<$100 mls) Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) technique is used.

Sample bags are leached for 24 hours with 1000 mls of 5% HNO_3. An aliquot of each sample is taken for analysis of all elements (except Zn) by GFAAS. Zn is analyzed by Flame Atomic Absorption. Both the sample and leachate values are reported as concentrations in units of mg/l.

For the ICP method, two QC standards (0.06 mg/l and 0.20 mg/l) are carried through the concentration procedures and analysed. Two filtered composites of cumulative samples are concentrated (one composite is spiked at a higher level) and analysed. The standard as well as the composite concentration must be within ±3 standard deviations of the mean values calculated from the previous analysis, otherwise samples are checked by GFAAS. Precision is calculated from the standard deviation of the difference between 3 duplicates per run at various concentration levels.

Quality control for the GFAAS method involves the analyses of calibration standards, three "check" standards, and two EPA (Environmental Protection Agency) solutions. Precision is calculated from the standard deviation of these two QC EPA solutions (one solution at the low end and one at the high end of the calibration curve) which are analysed with each set of standards.

Table 9 summarizes the precision of the ICP analytical method as well as providing blank levels for the procedure. All blank levels are at or below detection limits.

Precision is represented by the coefficient of variation (Standard Deviation/Mean x 100). The majority of parameters are precise within ±20%, however since metal analyses are reported near their detection limits, percentages become somewhat meaningless.

Table 10 summarizes the accuracy and between-run precision of the GFAAS analytical method. Precision and accuracy vary significantly according to the parameter type and the concentration level. Accuracies are all within ± 20% and precision (between-run) varies from ± 40% (Zinc) to ± 11% (Vanadium).

5.0 PRECISION AND ACCURACY ESTIMATES

Overall estimates (of the total measurement system) of precision and accuracy for the cumulative precipitation database during the 1980-81 sampling period are unavailable. The installation of colocated sites to determine overall precision and special studies to estimate precision and accuracy were initiated late in 1982. Although laboratory estimates are available, field estimates (sample collection, handling, storage etc.) will only be available for inclusion in the evaluation of the 1983 cumulative data.

6.0 SUMMARY AND RECOMMENDATIONS

The performance of the cumulative precipitation monitoring network from June 1980 to December 1981 was evaluated by using available field and office comments, validation flags and discrepancies, and laboratory quality control data. The following points summarize these findings:

1. A total of 503 samples were collected from 34 monitoring sites.
2. 22.7% of all samples had sampler malfunction codings.
3. 20.7% of all samples leaked .
4. 2.2% samples were lost, and 3.2% samples were not submitted.
5. Data recovery averaged 83.4%.
6. The average precipitation collector efficiency was 61.4% with seasonal averages of 71.3% for summer, and 53% for winter. Abnormal efficiencies were coded for 31.6% of all calculated sampler efficiencies.
7. 5.3% of all sample results were coded unreliable.
8. Conductivity discrepancies occurred in 8.8% of all samples, pH discrepancies in 11.3%, and ionic balance discrepancies in 4.6%.
9. All water quality analyses are estimated to be accurate within $\pm$ 15%. Precision estimates varied with parameter type but pH, total H^+, sulphate and nitrate were all within $\pm$ 5%.
10. Metals analyses accuracies using EPA references vary with parameter type but generally the majority of parameters were within $\pm$ 20%. Precision estimates are poorer due to extremely low concentrations (detection limits).

The cumulative precipitation network has undergone changes since its inception in 1980. New sampling bags and gapless knife-edge collars, revamped operating procedures, a preventive maintenance program and an extensive quality assurance program have been implemented. While some of these changes took effect during 1982, many were implemented during 1983. Improvements should be seen in the 1982 cumulative data in terms of sampler malfunctions and leaked samples. Estimates of precision and accuracy will also become available due to the installation of colocated sites, duplicate analyses, and other quality assurance activities after 1981.

In light of these improvements, several recommendations are provided to ensure the continued collection of quality data. These recommendations in order of priority are:

1. To investigate the causes of sampler malfunctions with special emphasis on the source and causes of blown fuses. Technicians are to identify the sources of malfunctions and if these sources cannot be identified, remove and replace the instruments.
2. To evaluate the data (1982) collected from Pickle Lake, Smith's Falls, Dalhousie Mills, and Moonbeam in order to determine the representativeness of these sites.
3. To evaluate the effectiveness of the new sampling bags by quantitatively comparing the frequency of the occurrences of leaks in the old and new bags.
4. To improve the measurement technique for cumulative gauge depths.
5. To investigate whether to discontinue the reporting of vanadium, nickel and cadmium since less than detection limits are reported consistently at all sites (or improve the sensitivity of the analytical technique).

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2. Bardswick, W. S., 1983: "APIOS Technical and Operating Manual". Ontario Ministry of the Environment, Air Resources Branch, April 1983.

3. Bardswick, W. S., 1984: "Quality Assurance Plan - APIOS Deposition Monitoring Program". Ontario Ministry of the Environment, Air Resources Branch. Report No. ARB 76-84-ARSP.

4. Kirk, R. W., 1983: "Data Validation Procedures - Cumulative Precipitation Monitoring Network", Ontario Ministry of the Environment, Air Resources Branch, May 1983.

Table 1. Site Identification Numbers

1. Colchestor
2. Merlin
3. Port Stanley
4. Wilkesport
5. Alvinston
6. Huron Park
7. Shallow Lake
8. Palmerston
9. Waterloo
10. Milton
11. Uxbridge
12. Coldwater
13. Campbellford
14. Kaladar
15. Smith's Falls
16. Dalhousie Mills
17. Golden Lake
18. Whitney
19. Wilberforce
20. Dorset
21. Mckellar
22. Mattawa
23. Killarney
24. Bear Island
25. Gowganda
26. Ramsey
27. Moonbeam
28. Attawapiskat
30. Nakina
31. Dorion
32. Quetico Centre
34. Experimental Lakes Area
35. Ear Falls
36. Pickle Lake

Table 2. Regional Sites

Region	Site Numbers	Total # Sites
Southwestern	1 to 9	9
Central	10 to 12, 18 to 20	6
Southeastern	13 to 17	5
Northeastern	21 to 28	8
Northwestern	30 to 32, 34 to 36	6

Table 3

Conductivity, pH, Ionic Balance Discrepancies and Unreliable Data

Site #	# Samples Analysed	% Conductivity	% pH	% Ionic Balance	% Unreliable
1	16	--	6.3	--	4.0
2	16	--	12.5	--	4.5
3	15	13.3	6.7	--	3.6
4	16	--	6.3	6.3	7.1
5	14	--	21.4	7.1	5.8
6	1	--	--	--	4.5
7	14	7.1	7.1	--	2.9
8	16	--	25.0	--	6.0
9	16	6.3	12.5	--	7.1
10	15	6.7	26.7	--	19.4
11	15	--	20.0	--	1.8
12	4	25.0	--	--	1.1
13	16	6.3	--	6.3	4.5
14	16	12.5	6.3	--	1.7
15	15	--	26.7	--	8.8
16	16	12.5	12.5	12.5	10.5
17	16	12.5	--	6.3	1.4
18	15	13.3	--	--	3.3
19	15	6.7	6.7	--	2.1
20	19	15.8	--	5.3	1.2
21	13	--	--	--	5.9
22	14	--	7.1	14.3	2.9
23	19	10.5	5.3	5.3	6.5
24	17	11.7	--	--	4.3
25	18	11.1	--	--	3.0
26	19	5.3	--	--	2.6
27	16	12.5	25.0	6.3	7.4
28	13	23.1	38.5	23.1	11.5
30	15	26.7	46.7	33.3	8.2
31	16	25.0	--	--	1.1
32	1	--	--	--	--
34	2	--	--	--	--
35	13	--	15.4	7.7	7.7
36	14	21.4	28.6	14.3	9.1

"--" denotes 0.0 %

Table 4

Comparison of Milton and Waterloo Data (1980-81)

Sample End Date	pH (lab)		Calcium (mg/l)		Magnesium (mg/l)		Potassium (mg/l)	
	M	W	M	W	M	W	M	W
Sept. '80	5.42	4.12	.69	.24	.230	.045	.030	0.30
Oct. '80	5.95	4.49	2.16	.38	.465	.055	.150	.030
Nov. '80	6.50	4.98	3.85	1.15	1.700	.290	.150	.180
Dec. '80	-	4.38	-	.53	-	.110	-	.020
Jan. '81	6.70	4.21	-	.34	-	.125	-	.060
Feb. '81	5.66	4.23	1.14	.12	.570	.015	.050	.010
Mar. '81	7.22	6.61	4.70	1.72	1.700	.600	.050	.040
Apr. '81	6.83	4.31	1.80	.49	.775	.095	.140	.050
May '81	4.06	4.00	.70	.92	.210	.330	.060	.130
June '81	4.54	4.20	.77	.30	.265	.080	.430	.030
July '81	4.49	3.98	.52	.30	.125	.055	.220	.020
Aug. '81	3.88	3.85	.29	.82	.065	.260	.040	.440
Sept. '81	4.17	6.50	.43	-	.140	-	.220	-
Oct. '81	4.28	6.75	.46	1.25	.135	.115	.020	.170
Nov. '81	6.06	4.88	.84	.79	.390	.240	.130	.040
Jan. '82	6.65	-	1.88	.98	.650	.360	.100	.070

M - Milton

W - Waterloo

"-" - Data Unavailable

Table 5

Unreliable Results vs Parameter

Parameter	# Unreliable results	% Unreliable results
Cond.	35	6.3
pH (lab)	86	15.4
Total H^+	4	0.7
Sulphate	12	2.1
Nitrate (as N)	14	2.5
Calcium	58	10.4
Chloride	33	5.9
Total Kjeldahl Nitrogen	29	5.2
Magnesium	59	10.5
Potassium	31	5.5
Sodium	43	7.7
Ammonium	28	5.0
Phosphate (as P)	24	4.3
Managanese	8	1.4
Nickel	3	0.5
Zinc	12	2.1
Iron	30	5.4
Lead	8	1.4
Alumium	27	4.8
Copper	9	1.6
Cadmium	7	1.3

Note: Vanadium is consistently reported at or below detection limits, therefore no validation checks have been applied.

Table 6

Laboratory Accuracy - Water Quality Parameters

Parameter	Units	Calibration Range	Resolution*	Quality Control Standard - A				Quality Control Standard - B			
				n	Theoretical Concentration	Mean Concentration Found	Percentage Difference	n	Theoretical Concentration	Mean Concentration Found	Percentage Difference
Conductivity	us/cm	0-100	1.5	54	73.9	73.8	0.1	54	14.9	16.5	10.7
pH	pH units	3.50 - 7.00	0.001	110	6.86	6.95	1.3	108	4.01	4.01	0
Total H+ (pH 8.3)	mg/l	0.2	0.0001	57	0.500	0.501	0.2	56	0.200	0.219	9.5
Sulphate	mg/l	0.07 - 10.0	0.1	177	8.00	7.99	0.1	177	2.00	2.02	1.0
Nitrate (N)	mg/l	0.02 - 2.00	0.02	167	1.60	1.60	0	165	0.40	0.40	0
Calcium	mg/l	0.02 - 2.00	0.02	36	1.20	1.22	1.7	36	0.20	0.20	0
Chloride	mg/l	0.03 - 1.50	0.02	138	1.20	1.20	0	138	0.30	0.30	0
Kjeldahl (asN)	mg/l	0.04 - 2.00	0.02	95	1.50	1.51	0.7	95	0.50	0.49	2.0
Magnesium	mg/l	0.01 - 0.50	0.005	21	0.300	0.294	2.0	21	0.050	0.047	6.0
Potassium	mg/l	0.02 - 1.00	0.01	21	0.600	0.603	0.5	21	0.100	0.097	3.0
Sodium	mg/l	0.01 - 1.00	0.01	36	0.600	0.600	0	37	0.100	0.098	2.0
Ammonium	mg/l	0.006 - 0.400	0.004	92	0.300	0.301	0.3	93	0.100	0.106	6.0
Phosphorous	mg/l	0.003 0 0.200	0.002	94	0.150	0.152	1.3	94	0.050	0.051	2.0

* Resolution is arbitrarily based on the readability of ± 1 line on a 100 line strip chart recorder (1% of full scale). In most cases, analysts can read to better than 1%.

Table 7

Laboratory Precision (within-run) - Water Quality Parameters

Parameter	Units	Concentration Range 0-20 % F.S. n	Mean	Standard Deviation	Coefficient of Variation %	Concentration Range 20-50% F.S. n	Mean	Standard Deviation	Coefficient of Variation %
Conductivity	us/cm	14	10.5	0.3	3	44	35.5	0.4	1
pH	pH units	0	-	-	-	3	4.37	0.023	-
Total H+ (pH 8.3)	mg/l	1	0.023	-	-	4	0.0814	0.00018	<1
Sulphate	mg/l	15	1.16	0.04	3	31	3.10	0.108	3
Nitrate (asN)	mg/l	12	0.25	0.01	4	19	0.70	0.016	2
Calcium	mg/l	25	0.187	0.011	6	10	0.690	0.026	4
Chloride	mg/l	17	0.160	0.015	9	9	0.501	0.013	3
Kjeldahl Nitrogen	mg/l	249	0.254	0.022	9	91	0.620	0.002	<1
Magnesium	mg/l	10	0.056	0.003	5	6	0.186	0.002	1
Potassium	mg/l	16	0.079	0.012	15	3	0.340	0.015	4
Sodium	mg/l	29	0.071	0.007	10	9	0.286	0.013	5
Ammonium (asN)	mg/l	-	-	-	-	3	0.742	0.010	1
Phosphorous	mg/l	266	0.017	0.002	12	50	0.066	0.0028	4

Table 8

Accuracy and Precision Summary

Water Quality Parameters

Parameter	Units	Accuracy Concentration	Accuracy ± %	Precision Concentration	Precision ± %
Conductivity	us/cm	15	11	10	3
pH	pH units	4.0	-	4.4	-
Total H+ (pH 8.3)	mg/l	0.2	10	0.1	1
Sulphate	mg/l	2.0	1	3.1	3
Nitrate (asN)	mg/l	0.4	1	0.3	4
Calcium	mg/l	0.2	1	0.2	6
Chloride	mg/l	0.3	1	0.2	9
Kjeldahl Nitrogen	mg/l	0.5	2	0.3	9
Magnesium	mg/l	0.05	6	0.06	5
Potassium	mg/l	0.1	3	0.08	15
Sodium	mg/l	0.1	2	0.1	10
Ammonium (asN)	mg/l	0.3	1	0.7	1
Phosphorous	mg/l	0.05	2	0.02	12

Table 9

Summary of Precision of the ICP Analytical Method - Blank and Duplicate Data

Parameter Units: mg/l	Sample Conc. Range	n	Mean	Standard Deviation	Coefficient of Variation	n	Blank Levels Mean	Std. Dev.
Manganese	0 - .010	63	.0039	.0005	13	30	<.001	<.001
Nickel	0 - .002	61	.00065	.00031	48	28	<.001	<.001
Zinc	0 - .020	68	.0066	.0011	17	28	<.002	<.002
Iron	040 - .100	23	.061	.010	16	26	.001	.001
Lead	0 - .020	74	.0064	.0018	28	30	<.001	<.001
Vanadium	0 - .0008	64	.0003	.0001	33	30	<.0002	<.0002
Aluminum	0 - .040	37	.0233	.0059	25	30	.002	.004
Copper	0 - .012	69	.00245	.00064	26	26	<.001	<.001
Cadmium	0 - .0008	70	.0002	.0001	50	30	<.0001	<.0001

Table 10

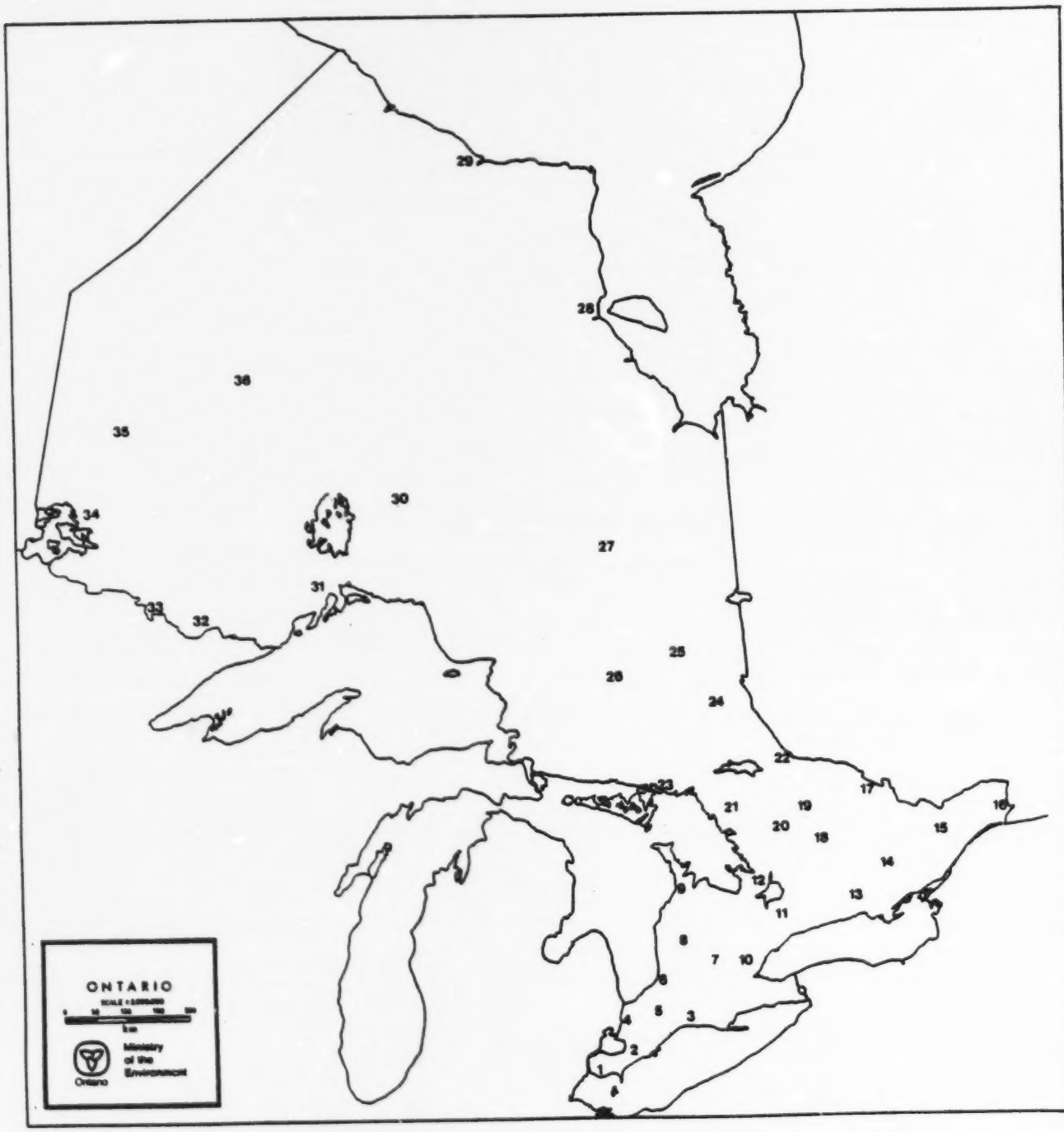
Summary of Precision and Accuracy of GFAAS Analytical Method

Parameter Units: mg/l	n	True Value EPA Solt'n	Mean Concentration Found	Percentage Difference	Standard Deviation	Coeff. of Variation	n	BLANK LEVELS Mean	BLANK LEVELS Standard Deviation
Manganese	26	0.0048	0.005	4.2	0.001	20	10	<.001	<.001
Nickel	13	0.0016	0.0019	18.8	0.0006	32	10	<.001	<.001
Zinc*	8	0.0048	0.005	4.2	0.002	40	10	<.002	<.002
Iron	24	0.039	0.043	10.3	0.003	7	10	0.003	0.002
Lead	19	0.0038	0.0043	13.2	0.0007	16	10	0.001	0.001
Vanadium	12	0.0085	0.009	5.9	0.001	11	10	<.002	<.002
Aluminum	27	0.0085	0.010	17.6	0.003	30	10	<.005	<.005
Copper	26	0.0037	0.003	18.9	0.001	67	10	0.001	0.001
Cadmium	23	0.00059	0.0006	1.7	0.0001	17	10	<.0001	<.0001

* Zinc analysed by Flame AAS not GFAAS.

Sept.6/84
6AR16-19

Fig.1 Station Location Map
Cumulative Network



1 - COLCHESTER
2 - MERLIN
3 - PORT STANLEY
4 - WILKESPORT
5 - ALVINSTON
6 - HURON PARK
7 - WATERLOO
8 - PALMERSTON
9 - SHALLOW LAKE
10 - MILTON
11 - UXBRIDGE
12 - COLDWATER
13 - CAMPBELLFORD
14 - KALADAR
15 - SMITH'S FALLS
16 - DALHOUSIE MILLS
17 - GOLDEN LAKE
18 - WILBERFORCE
19 - WHITNEY
20 - DORSET
21 - MCKELLAR
22 - MATTAWA
23 - KILLARNEY
24 - BEAR ISLAND
25 - GOWGANDA
26 - RAMSEY
27 - MOONBEAM
28 - ATTAWAPISKAT
29 - WINISK
30 - NAKINA
31 - DORION
32 - QUETICO CENTRE
33 - LAC LA CROIX
34 - EXP. LAKES AREA
35 - EAR FALLS
36 - PICKLE LAKE

Fig. 2

Site vs. Sampler Malfunction

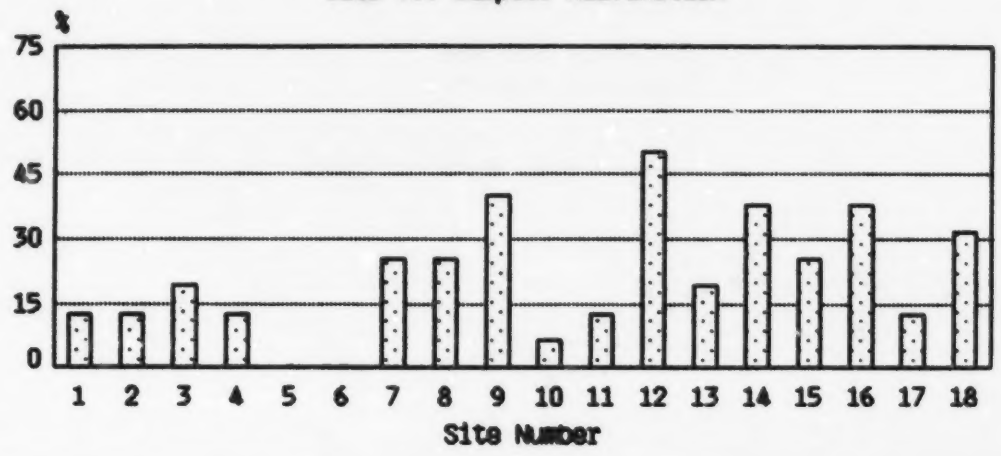
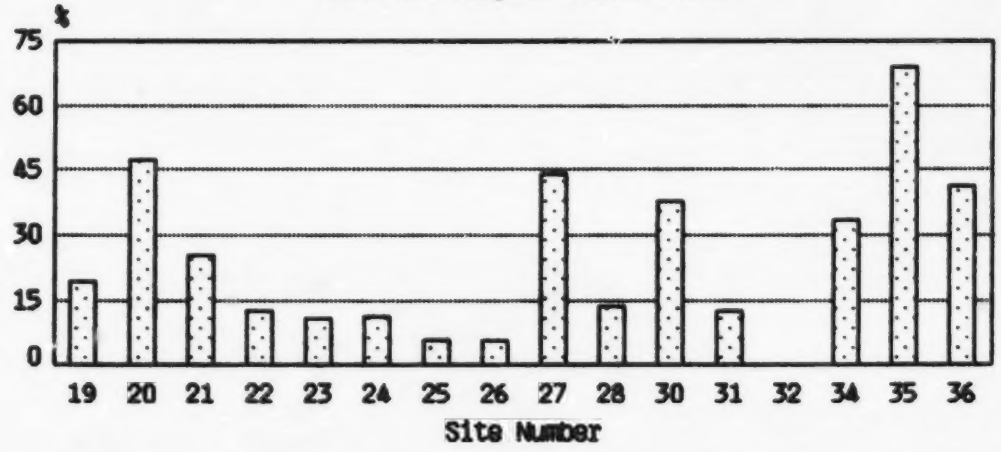


Fig. 2

Site vs. Sampler Malfunction



1	12.5	13	18.8	25	5.6
2	12.5	14	37.5	26	5.3
3	18.8	15	25	27	43.8
4	12.5	16	37.5	28	13.3
5	0	17	12.5	30	37.5
6	0	18	31.3	31	12.5
7	25	19	18.8	32	0
8	25	20	47.4	34	33.3
9	40	21	25	35	68.8
10	6.3	22	12.5	36	41.2
11	12.5	23	10.5		
12	50	24	11.1		

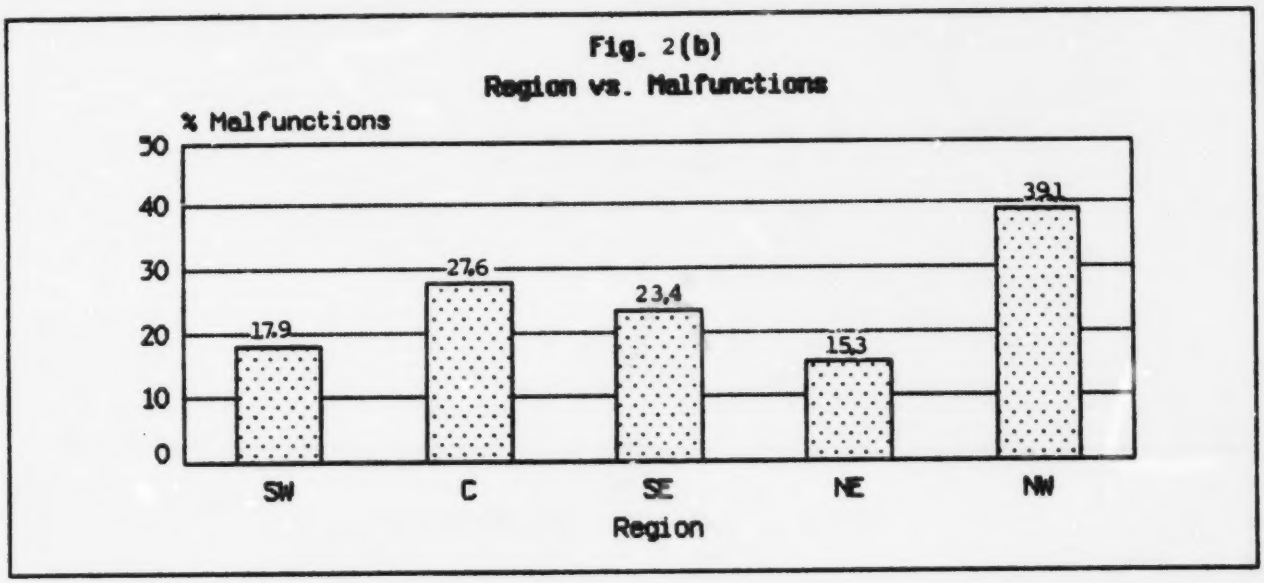


Fig. 2(b)
Region vs. Malfunctions
% Malfunctions
50
40
30
20
10
0
17.9
27.6
23.4
15.3
39.1
SW
C
SE
NE
NW
Region

Fig.3

Sampler Malfunction Histogram

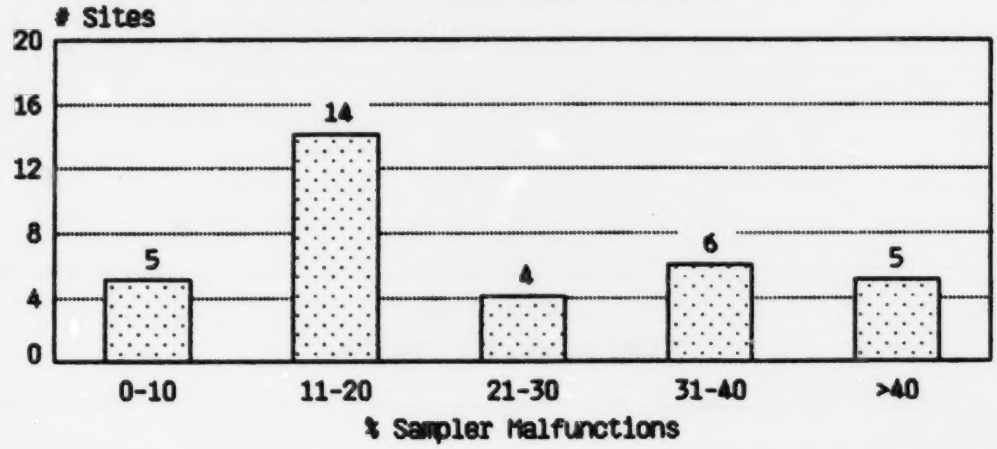
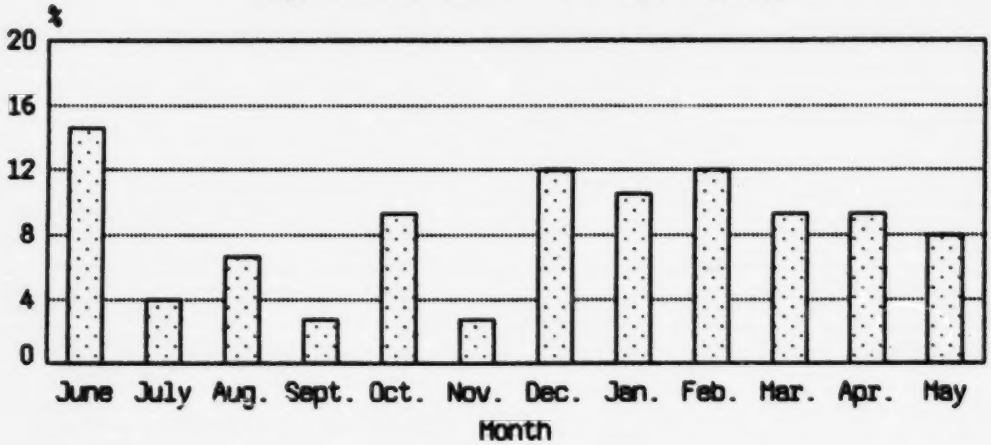


Fig. 4

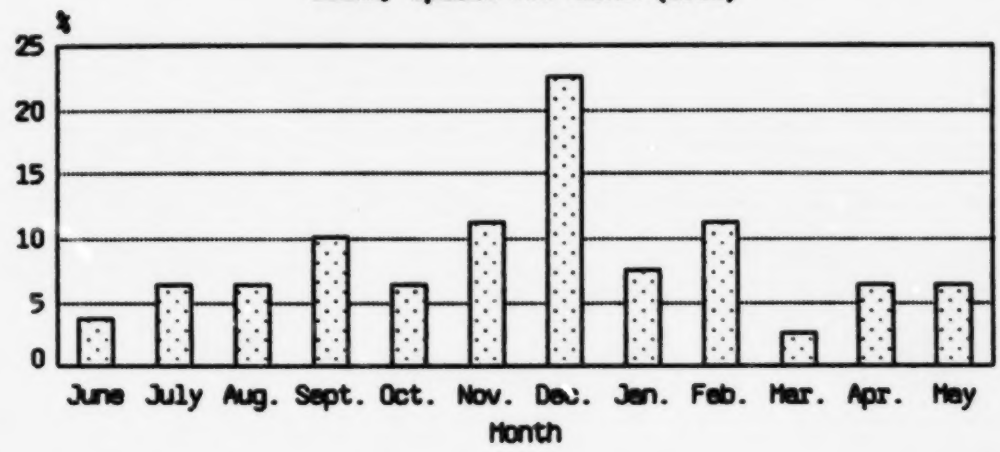
Sampler Malfunction vs. Month (1981)



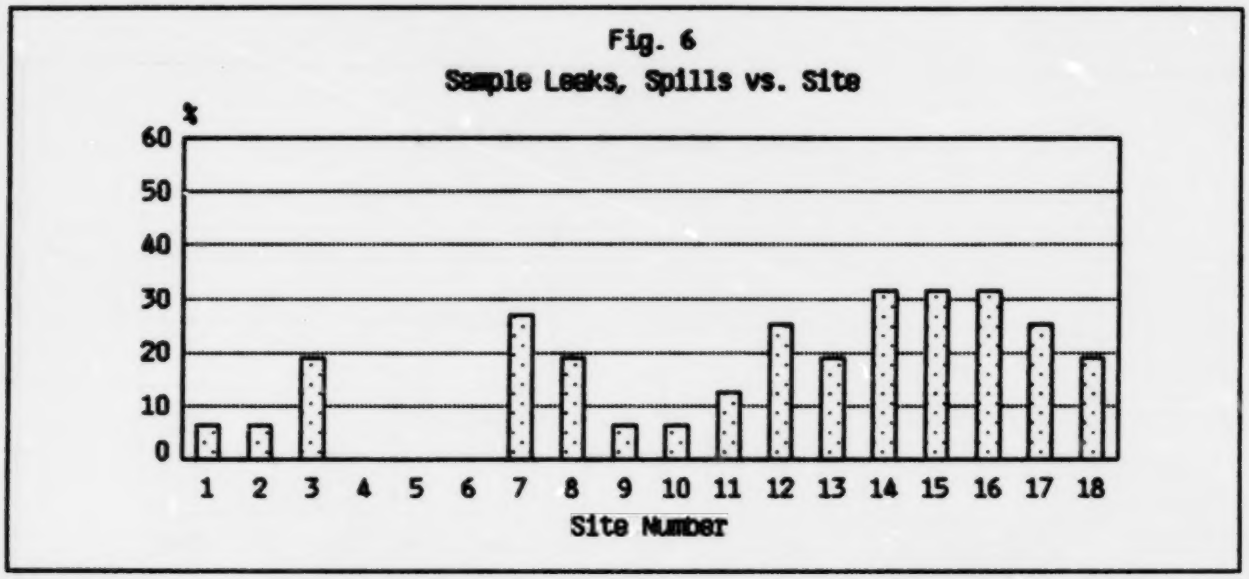
June	14.5
July	3.9
Aug.	6.6
Sept.	2.6
Oct.	9.2
Nov.	2.6
Dec.	11.9
Jan.	10.5
Feb.	11.9
Mar.	9.2
Apr.	9.2
May	7.9

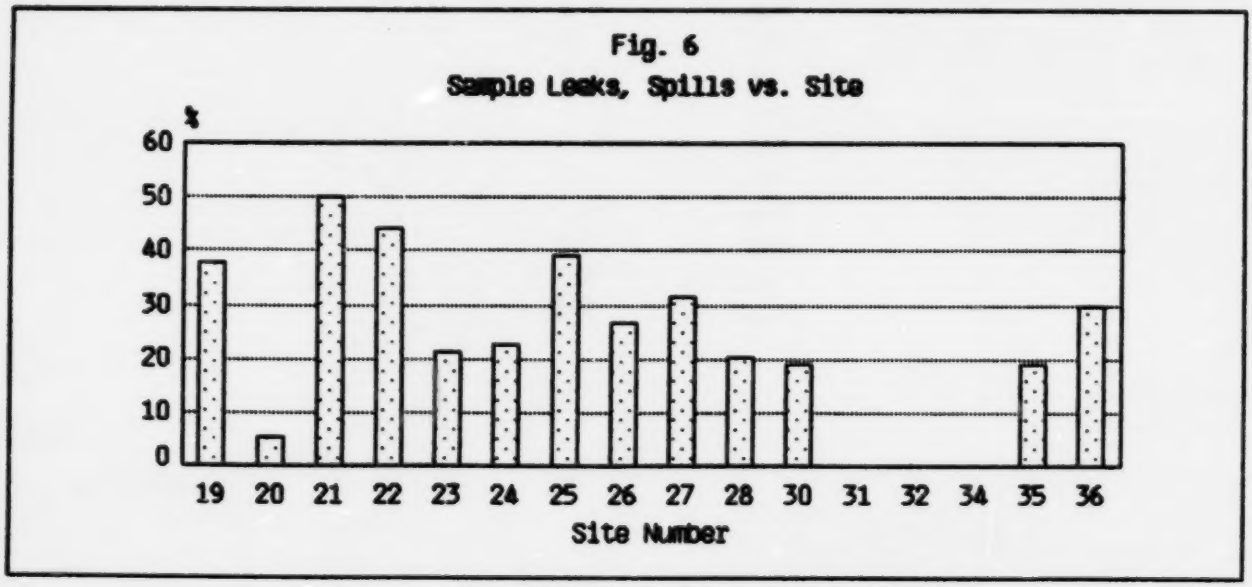
Fig. 5

Leaks, Spills vs. Month (1981)



June	3.8
July	6.3
Aug.	6.3
Sept.	10
Oct.	6.3
Nov.	11.3
Dec.	22.5
Jan.	7.5
Feb.	11.3
Mar.	2.5
Apr.	6.3
May	6.3

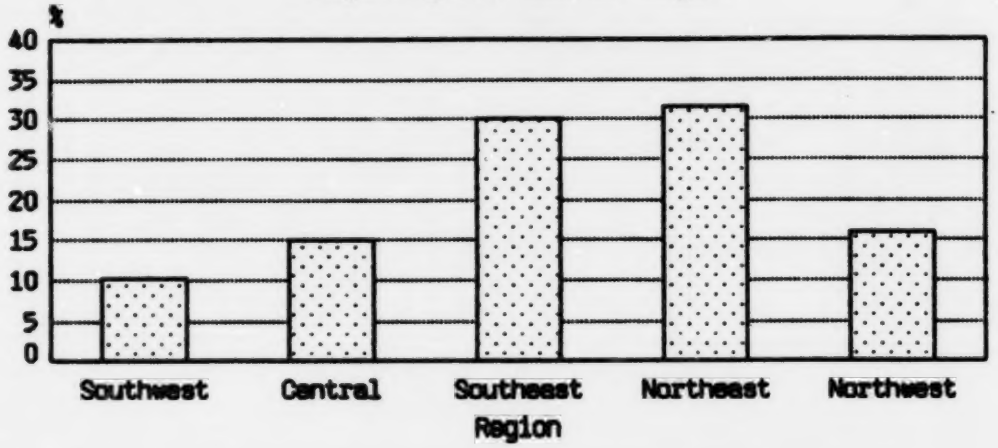




1	6.3	10	6.3	19	37.5	28	20
2	6.3	11	12.5	20	5.3	30	18.8
3	18.8	12	25	21	50	31	0
4	0	13	18.8	22	43.8	32	0
5	0	14	31.3	23	21.1	34	0
6	0	15	31.3	24	22.2	35	18.8
7	26.7	16	31.3	25	38.9	36	29.4
8	18.8	17	25	26	26.3		
9	6.3	18	18.8	27	31.3		

Fig. 7

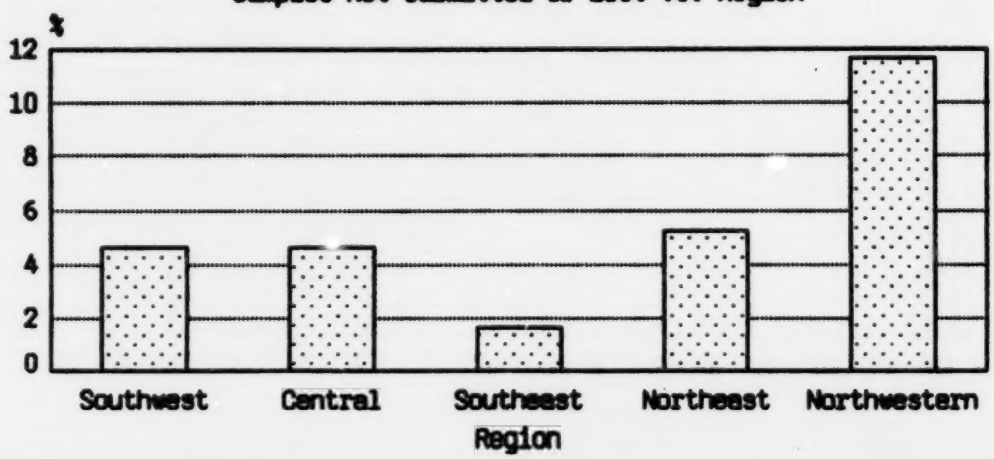
Samples Spill, Leak vs. Region



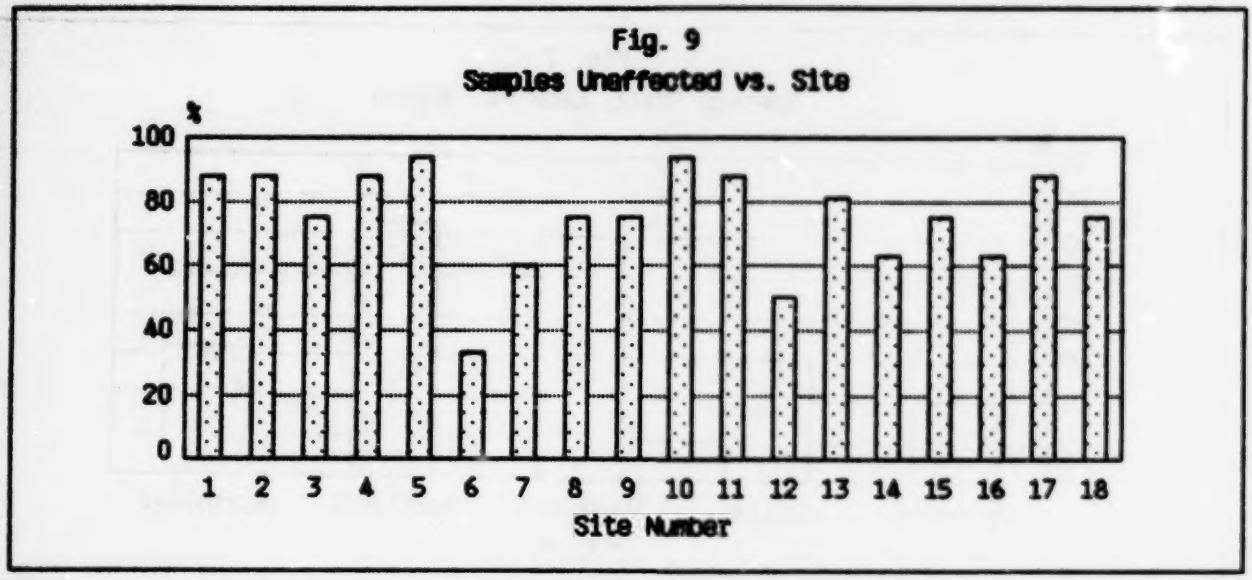
Southwest	10
Central	14.9
Southeast	30
Northeast	31.4
Northwest	15.9

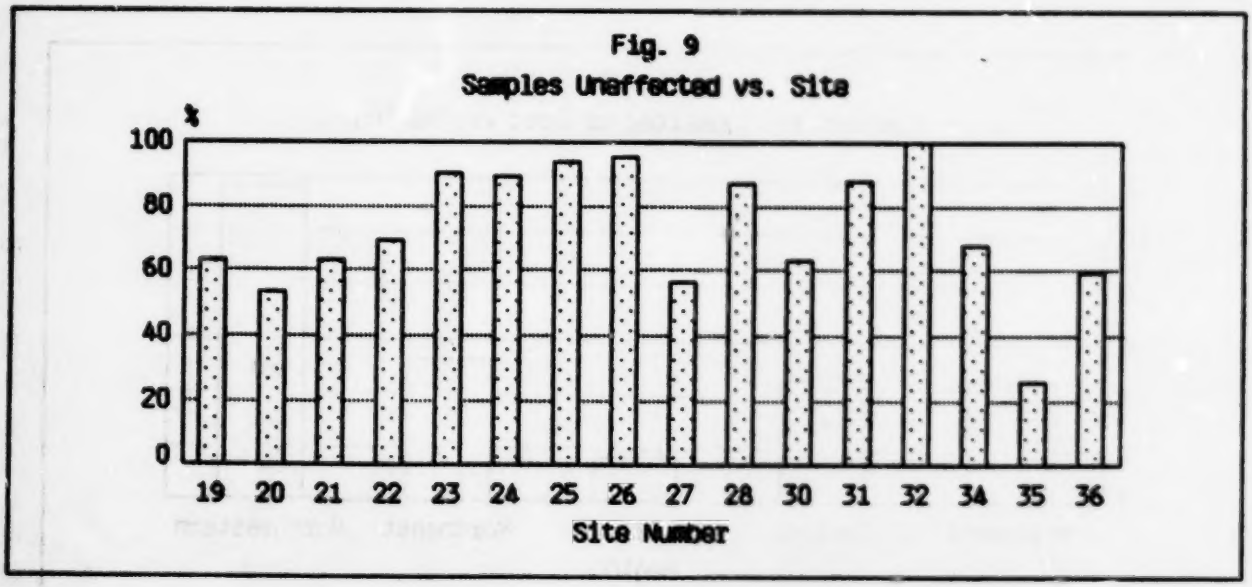
Fig. 8

Samples Not Submitted or Lost vs. Region

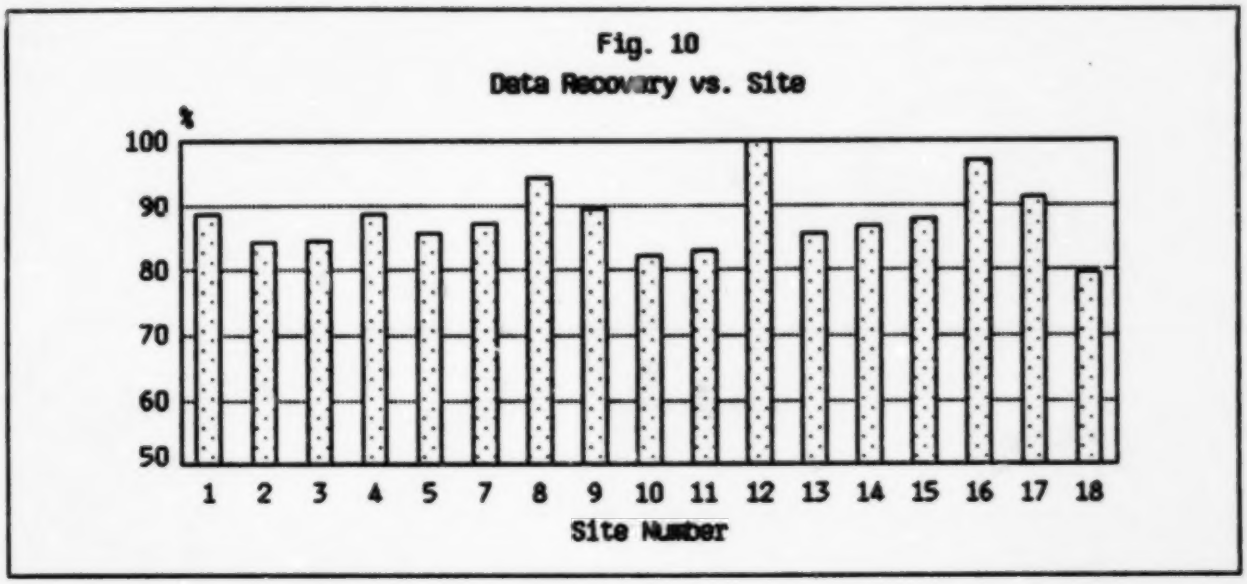


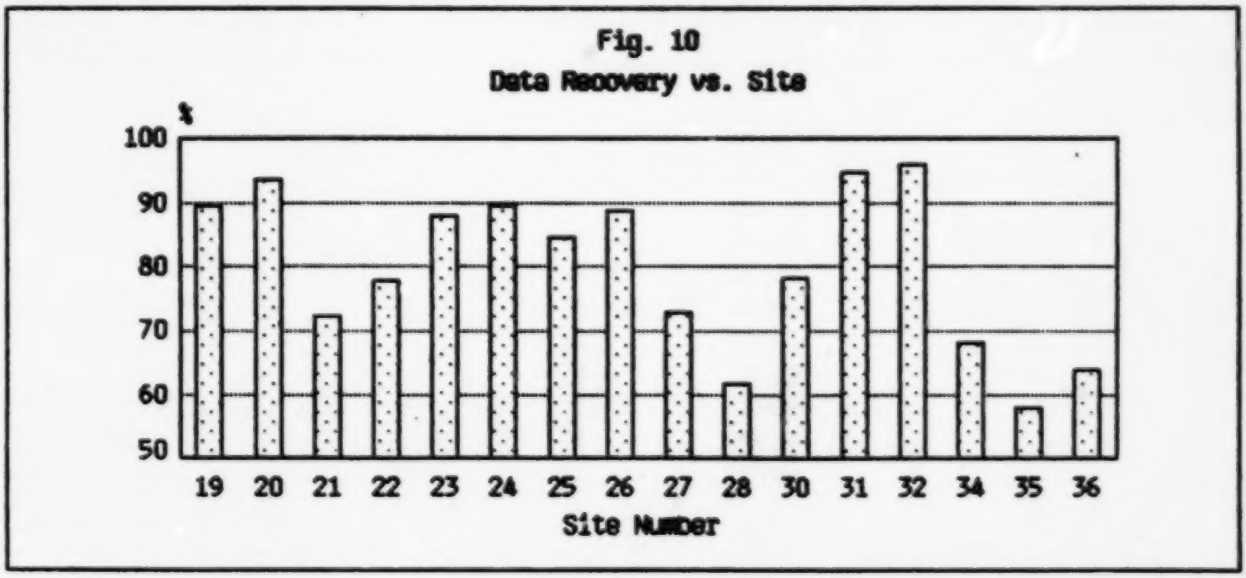
Southwest	4.6
Central	4.6
Southeast	1.6
Northeast	5.2
Northwest	11.6



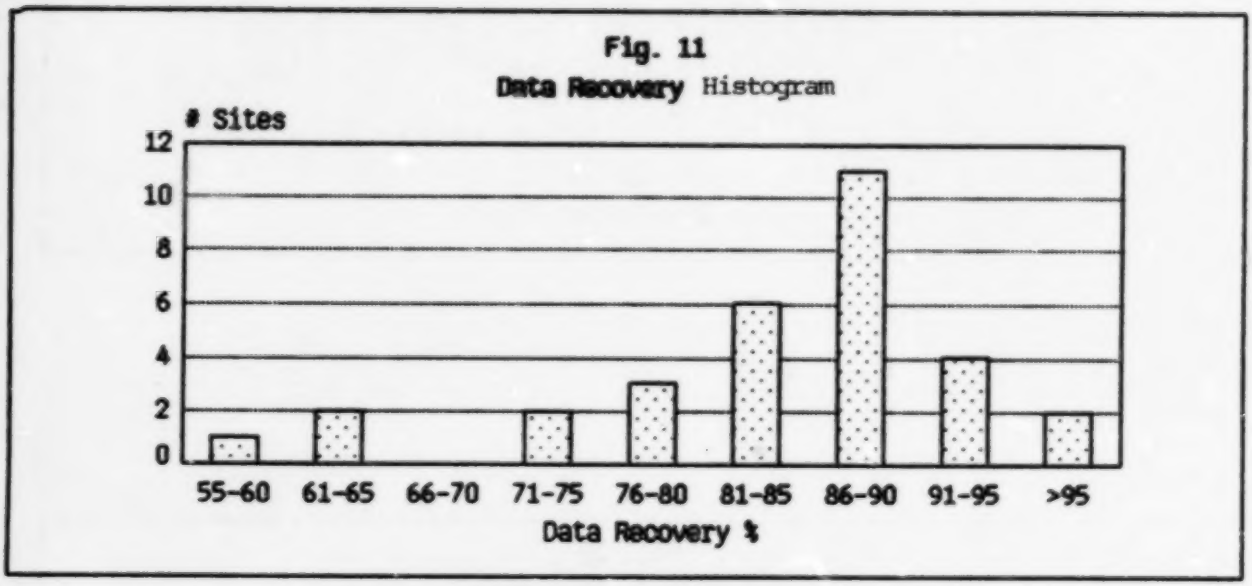


1	88	10	94	19	63	28	87
2	88	11	88	20	53	30	63
3	75	12	50	21	63	31	88
4	88	13	81	22	69	32	100
5	94	14	63	23	90	34	67
6	33	15	75	24	89	35	25
7	60	16	63	25	94	36	59
8	75	17	88	26	95		
9	75	18	75	27	56		

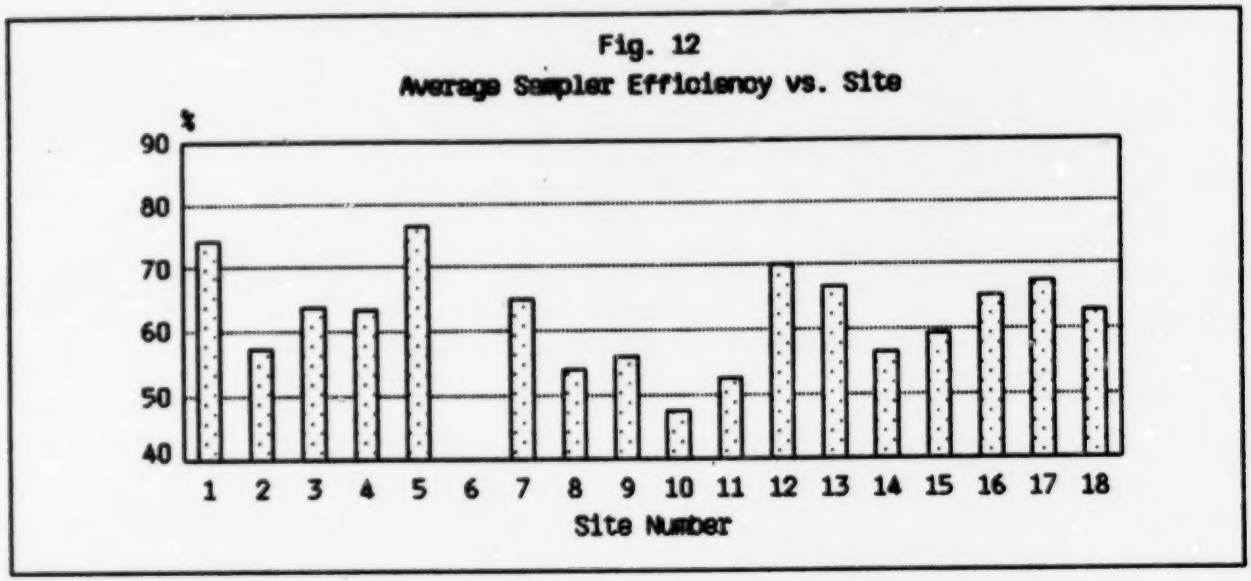


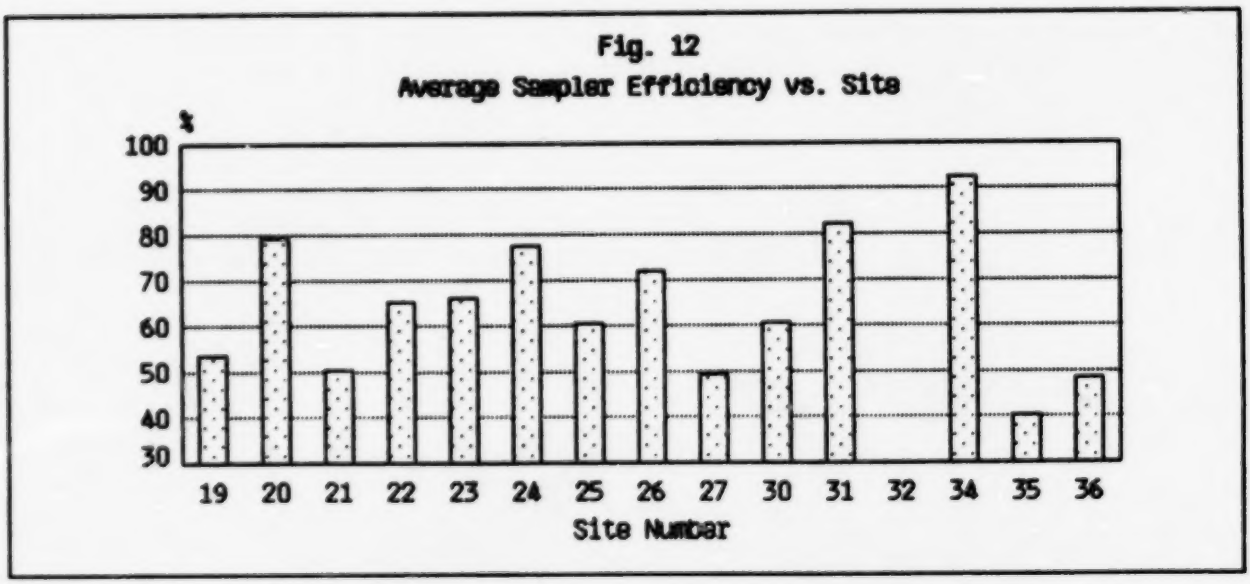


1	88.5	10	82	19	89.3	28	61.7
2	84.1	11	82.8	20	93.6	30	77.9
3	84.6	12	100	21	72.1	31	94.5
4	88.5	13	85.4	22	77.6	32	95.8
5	85.7	14	86.5	23	87.9	34	68.1
7	86.9	15	87.8	24	89.4	35	57.8
8	94.3	16	96.9	25	84.5	36	63.7
9	89.3	17	91.1	26	88.6		
		18	79.4	27	72.7		

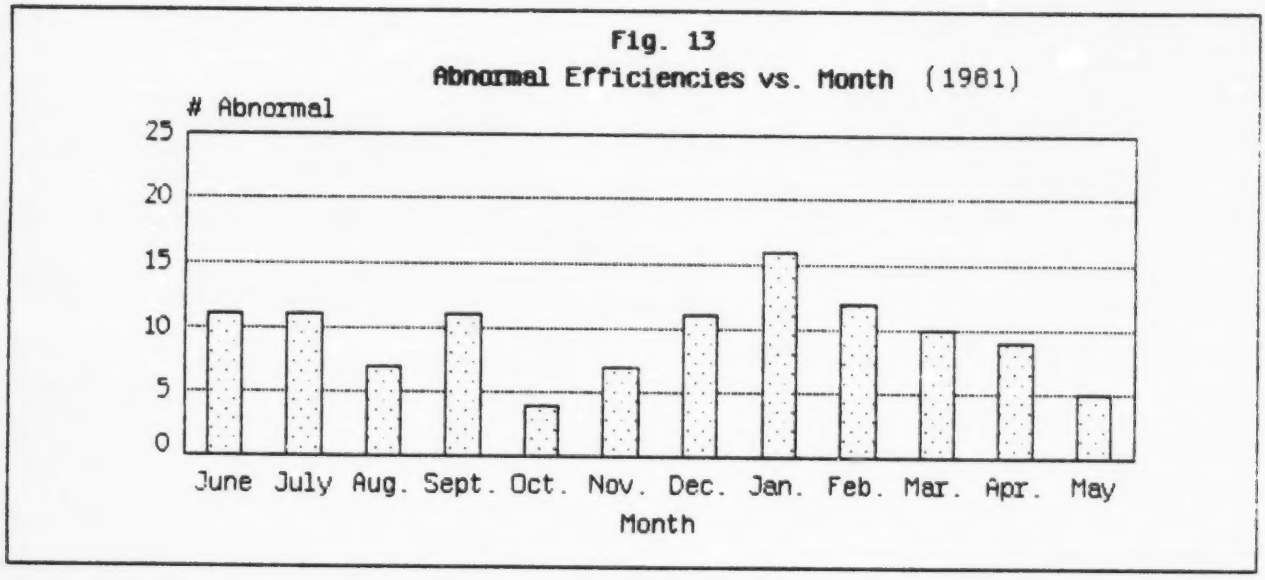


55-60	1
61-65	2
66-70	0
71-75	2
76-80	3
81-85	6
86-90	11
91-95	4
>95	2



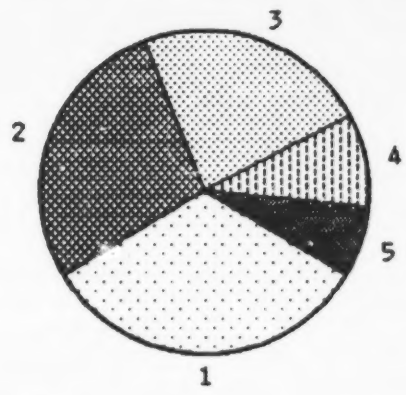


1	74.2	10	47.4	19	53.7	30	60.6
2	57.1	11	52.3	20	79.2	31	81.9
3	63.7	12	70.1	21	50.3	32	-
4	63.3	13	66.5	22	65	34	92.3
5	76.4	14	56.4	23	65.9	35	40.3
6	-	15	59.2	24	77.4	36	48.3
7	64.7	16	65	25	60.2		
8	53.9	17	67.3	26	71.9		
9	55.8	18	62.7	27	49.5		



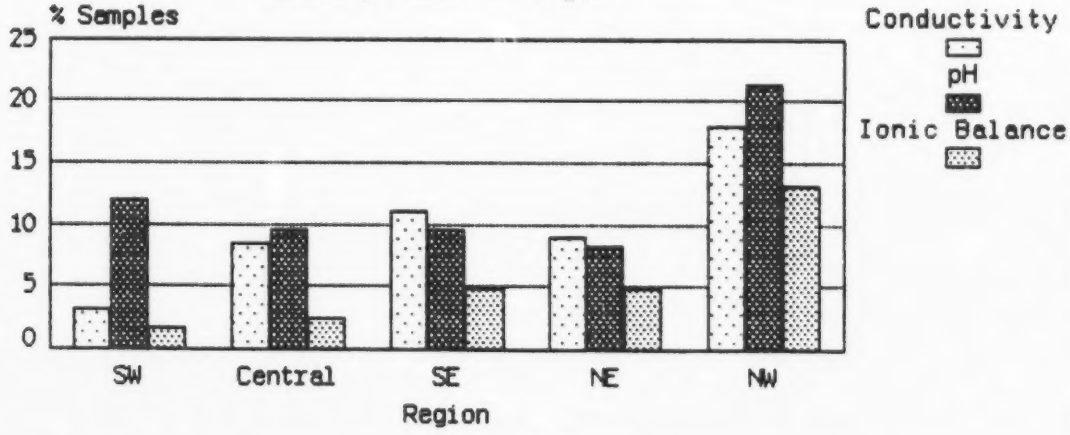
June	11
July	11
Aug.	7
Sept.	11
Oct.	4
Nov.	7
Dec.	11
Jan.	16
Feb.	12
Mar.	10
Apr.	9
May	5

Fig. 14
Causes of Abnormal Efficiencies: Sept. 80 to Dec. 81



1	NO EXPLANATION	32.6%
2	SAMPLE SPILL OR LEAK	28%
3	SAMPLER MALFUNCTION	22.7%
4	INCORRECT VOLUME	9.9%
5	WATER IN DRY BAG	6.8%

Fig. 15
Discrepancies vs. Region



	Cond.	pH	Ionic B.
Southwestern	3.2	12.1	1.6
Central	8.4	9.6	2.4
Southeastern	11.1	9.5	4.8
Northeastern	9	8.3	4.8
Northwestern	18	21.3	13.1

APPENDIX 1

Quality Control Data - Water Quality Section

Test Name: CONDUCTIVITY

Lab.: PR

Units: µS/cm

Period: from 10/01/80 to 25/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: The sample is introduced into a jacketed conductivity cell and equilibrated to 25 °C.

Instrumentation: Radiometer CDM3 Conductivity meter with a 324 jacketed conductivity cell.

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
0 - 100	0 - 150	1.5	0

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	54	73.90	73.819	-0.081	1.7389
B	54	14.94	16.471	1.531	0.6523
Long Term Blank:					
A+B	54	88.84	90.270	1.430	1.8851
A-B	54	58.96	57.367	-1.593	1.8222

A+B: calc. WL 3.64 CL 5.47 actual WL 3.75 CL 5.64

A-B: calc. WL 3.64 CL 5.47 actual WL 3.75 CL 5.64

Std. Dev.: within, S_w = 1.2885 between, S = 1.3109 S/S_w = 1.02

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					

R_1+R_2 calc. WL CL actual WL CL

R_1-R_2 calc. WL CL actual WL CL

Std. Dev.: within, S_w= between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	14	44	4	62
Std. Dev.:	0.260	0.401	0.408	0.370
Mean:	10.5	35.5	67.5	31.9
% RSD: 3.6%		Detection Criteria: 0.304*		

* Based on old data.

Test Name: pH

Units: pH units

Lab.: PR

Period: from 02/01/80 to 31/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: pH is directly measured on a stirred aliquot of sample (100 mL) at room temperature. Stirring rate, beaker size, degree of electrode immersion and temperature range are all strictly defined. For samples with low volumes, the test is done in 20 mL plastic sample cups with stirring.

Instrumentation: Radiometer pHM64 meter with a combination electrode (GK2401C).

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
3.50 - 7.00	-	0.001	1

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	110	6.86	6.950	-0.001	0.0092
B	108	4.008	4.008	0.000	0.0081
Long Term Blank:					
A+B	108	10.87	10.867	-0.001	0.0140
A-B	108	2.85	3.851	-0.001	0.0101

A+B: calc. WL 0.020 CL 0.030 actual WL 0.020 CL 0.030

A-B: calc. WL 0.020 CL 0.030 actual WL 0.020 CL 0.030

Std. Dev.: within, S_w = 0.0072 between, S = 0.0086 S/S_w = 1.21

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					

R_1+R_2 calc. WL CL actual WL CL

R_1-R_2 calc. WL CL actual WL CL

Std. Dev.: within, S_w = between, S = S/S_w =

Range 0 - 14

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	0	3	0	3
Std. Dev.:	-	0.023	-	0.023
Mean:	-	4.37	-	4.37

% RSD: - Detection Criteria: -

Test Name: ACIDITY **Lab.:** PR

Units: mg/L as $CaCO_3$ **Periods:** from 12/09/80 to 31/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: Sample aliquots (100 mL) are titrated with 0.01N sodium hydroxide to a pH endpoint of 8.3. The titrant normality is determined by titrating 0.005N KHP to the same pH 8.3 endpoint. Titrant delivery is controlled by the first derivative of the titration curve and the stability of the pH readings following each aliquot of titrant.

Instrumentation: pHM64 pH meter; ABU80 autoburette, TRS-80; in-house interface box.

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
<10.0	-	0.005	1

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	57	25.0	25.04	0.04	0.267
B	56	10.0	10.96	0.96	0.270
Long Term Blanks:					
A+B	56	35.0	36.00	1.00	0.409
A-B	56	15.0	14.00	-0.92	0.346

A+B: calc. WL 0.69 CL 1.0 actual WL 0.70 CL 1.00

A-B: calc. WL 0.69 CL 1.0 actual WL 0.70 CL 1.00

Std. Dev.: within, S_w = 0.245 between, S = 0.268 S/S_w = 1.10

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					

R_1+R_2 calc. WL CL actual WL CL

R_1-R_2 calc. WL CL actual WL CL

Std. Dev.: within, S_w = between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	1	4	3	8
Std. Dev.:	-	0.009	0.229	0.155
Mean:	1.15	4.07	6.15	4.49
% RSD: 3%		Detection Criteria: -		

Test Name: SULPHATE - DIONEX - AUTOMATED

Lab.: PR

Units: mg/L as SO_4

Period: from 02/01/80 to 30/12/80

Sample Type: Precipitation; some Rivers, Lakes

Sample Preparation:

Analytical Procedure: Sulphate is separated from other anions in the sample by ion chromatography using a mixture of 0.003M sodium bicarbonate and 0.0024M sodium carbonate as the eluent. After conversion to the acid form, the concentration of sulphate is determined from the conductivity of the sulphuric acid produced. Manually drawn concentration curves are used.

Instrumentation: Dionex Ion Chromatograph Model 10 modified to be compatible with an automated sampling train. Technicon sampler, AA-1 peristaltic pump; a timer (Supergrator III); control box (in-house design); Linear recorder.

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
0.07 to 10.0	0 - 10 µS/cm	0.1	6

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	177	8.0	7.99	-0.01	0.081
B	177	2.0	2.02	0.02	0.047
Long Term Blank:					
A+B	177	10.0	10.01	0.01	0.106
A-B	177	6.0	5.97	-0.03	0.080
A+B: calc. WL 0.16	CL 0.24	actual WL -		CL -	
A-B: calc. WL 0.16	CL 0.24	actual WL -		CL -	

Std. Dev.: within, S_w = 0.057 between, S = 0.067 S/S_w = 1.17

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					
R_1+R_2 calc. WL	CL	actual WL		CL	
R_1-R_2 calc. WL	CL	actual WL		CL	

Std. Dev.: within, S_w= between, S = S/S_w =

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	15	31	7	53
Std. Dev.:	0.040	0.108	0.104	0.095
Mean:	1.16	3.10	5.93	2.92
% RSD: 1.3%				

Detection Criteria: 0.07

Test Name: NITRATE - DIONEX - AUTOMATED

Units: mg/L as N

Lab.: PR

Period: from 02/01/80 to 30/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: Nitrate is separated from other anions in the sample by ion chromatography using a mixture of 0.003M sodium bicarbonate and 0.0024M sodium carbonate as the eluent. After conversion to the acid form nitrate is estimated by measuring the conductivity of the nitric acid produced. Manually drawn calibration curves are used.

Instrumentation: Dionex Ion Chromatograph Model 10 modified to be compatible with an automated sampling train. Technicon sampler; AA-1 peristaltic pump; timer (Supergrator III); control box (in-house design); Linear recorder.

Calibration:

Conc. Range	Operating Scale	-	Resolution	#Stds.
0.02 to 2.00	0 - 10.0 µS/cm		0.02	6

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	167	1.60	1.603	0.003	0.0199
B	165	0.40	0.404	0.004	0.0097
Long Term Blank:					
A+B	165	2.00	2.007	0.007	0.0267
A-B	165	1.20	1.198	-0.002	0.0168
A+B: calc. WL	0.03	CL 0.05	actual WL -	CL -	
A-B: calc. WL	0.03	CL 0.05	actual WL -	CL -	

Std. Dev.: within, S_w = 0.0119 between, S = 0.0158 S/S_w = 1.33

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					
R_1+R_2 calc. WL		CL	actual WL	CL	
R_1-R_2 calc. WL		CL	actual WL	CL	

Std. Dev.: within, S_w = between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	12	19	13	44
Std. Dev.:	0.010	0.016	0.032	0.022
Mean:	0.247	0.704	1.37	0.776
% RSD: 2.1%		Detection Criteria: 0.016		

Test Name: CALCIUM

Units: mg/L

Lab.: PR

Period: from 05/01/80 to 31/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: Samples are analyzed by AAS at 422.7 nm with an air-acetylene flame. Lanthanum (in dilute HCl solution) is introduced with an automated sampling train. Chart recorder results are converted to concentration by means of manually prepared calibration curves.

Instrumentation: Technicon Large Industrial Model Sampler; Gilson peristaltic pump; Varian AA175 (AAS), Linear recorder.

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
0.02 to 2.00	0.17 Abs.	0.02	6

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	36	1.20	1.218	0.018	0.0227
B	36	0.20	0.198	-0.002	0.0115
Long Term Blank:					
A+B	36	1.40	1.416	0.016	0.0283
A-B	36	1.00	1.020	0.020	0.0221

A+B: calc. WL 0.044 CL 0.066 actual WL 0.040 CL 0.060

A-B: calc. WL 0.044 CL 0.066 actual WL 0.040 CL 0.060

Std. Dev.: within, S_w = 0.156 between, S = 0.180 S/S_w = 1.15

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					

R_1+R_2 calc. WL CL actual WL CL

R_1-R_2 calc. WL CL actual WL CL

Std. Dev.: within, S_w = between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	25	10	5	40
Std. Dev.:	0.011	0.026	0.031	0.021
Mean:	0.187	0.690	1.44	0.470

% RSD: 2.1% Detection Criteria: 0.019

Test Name: CHLORIDE - DIONEX - AUTOMATED
Lab.: PR
Units: mg/L
Period: 08/01/80 to 30/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: Chloride is separated from other anions in the sample by ion chromatography using a mixture of 0.003M sodium bicarbonate and a 0.0024M sodium carbonate as the eluent. After conversion to the acid form, the concentration of chloride is determined from the conductivity of the hydrochloric acid produced. Manually drawn calibration curves are used.

Instrumentation: Dionex Ion Chromatography Model 10 modified to be compatible with an automated sampling train. Technicon sampler; AAI peristaltic pump; timer (Supergrator III); and control box (in-house design); Linear recorder.

Calibration:

Conc. Range	Operating Scale		Resolution	#Stds.
0.03 to 1.50	0 - 10 µS/cm	-	0.02	6

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	138	1.20	1.196	-0.004	0.0200
B	138	0.30	0.296	-0.004	0.0133
Long Term Blank:					
A+B	136	1.50	1.492	-0.008	0.0255
A-B	136	0.90	0.900	0.000	0.0219
A+B: calc. WL	0.044	CL 0.066	actual WL -	CL -	
A-B: calc. WL	0.044	CL 0.066	actual WL -	CL -	

Std. Dev.: within, S_w = 0.0155 between, S = 0.0168 S/S_w = 1.09

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					
R_1+R_2 calc. WL		CL	actual WL	CL	
R_1-R_2 calc. WL		CL	actual WL	CL	

Std. Dev.: within, S_w= between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	17	9	8	34
Std. Dev.:	0.015	0.013	0.012	0.014
Mean:	0.160	0.501	1.04	0.457
% RSD: 1.0%		Detection Criteria: 0.025		

Test Name: TOTAL KJELDAHL NITROGEN **Lab.:** RL

Units: mg/L as N **Period:** from 02/07/80 to 30/12/80

Sample Type: Rivers, Lakes

Sample Preparation:

Analytical Procedure: Samples are digested in a sulphuric acid-mercuric oxide-potassium sulphate media using two block digesters kept at 200 C and 360 C. The digestate is pH adjusted in line and the ammonia content is determined by formation of indophenol blue in a buffered system using nitroprusside as a catalyst. Total phosphorus is analyzed simultaneously.

Instrumentation: Basic AAII AutoAnalyzer system plus two Technicon BD40 block digesters plus a heating bath module (7.7 ml delay coil ast 38 C). Std cal (std dev) = 3.01 (0.466); 630 nm; 1.5 cm flow cell.

Calibration:

Conc. Range	Operating Scale		Resolution	#Stds.
0.04 to 2.00	0 to 0.5 Abs.	-	0.02	2

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	95	1.50	1.509	0.009	0.0172
B	95	0.50	0.494	-0.006	0.0100
Long Term Blank:	89	-	0.004	-	0.0138
A+B	95	2.00	2.003	0.003	0.0217
A-B	95	1.00	1.014	0.014	0.0179
A+B: calc. WL	0.036	CL 0.054	actual WL 0.040	CL 0.060	
A-B: calc. WL	0.036	CL 0.054	actual WL 0.040	CL 0.060	

Std. Dev.: within, S_w = 0.0127 between, S = 0.0141 S/S_w = 1.11

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R^1	188	1.40	1.399	-0.001	0.0294
R^2	190	0.84	0.842	0.002	0.0221
Digested Blanks:	95	-	0.0181	-	0.0127
R^1+R^2	95	2.24	2.240	0.000	0.0437
R^1-R^2	95	0.56	0.552	-0.008	0.0305
R^1+R^2 calc. WL	0.062	CL 0.092	actual WL -	CL -	
R^1-R^2 calc. WL	0.062	CL 0.092	actual WL -	CL -	

Std. Dev.: within, S_w = 0.0216 between, S = 0.0266 S/S_w = 1.24

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	249	91	15	355
Std. Dev.:	0.022	0.022	0.032	0.023
Mean:	0.254	0.620	1.32	0.393

% RSD: 2.13% Detection Criteria: 0.036

Test Name: MAGNESIUM

Lab.: PR

Units: mg/L

Period: from 29/05/80 to 22/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: Samples are analyzed by AAS at 285.2 nm with an air-acetylene flame. Lanthanum in dilute HCl solution is added by an automated sampling train. Chart recorder results are converted to concentration by means of manually prepared calibration curves.

Instrumentation: Technicon Sampler; Gilson peristaltic pump; Varian AA275 (AAS); Linear recorder.

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
0.01 to 0.50	0 - 0.4 Abs.	0.005	6

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	21	0.300	0.2936	-0.0064	0.00504
B	21	0.050	0.0467	-0.0033	0.00289
Long Term Blanks:					
A+B	21	0.350	0.3402	-0.0098	0.00602
A-B	21	0.250	0.2469	-0.0031	0.00558

A+B: calc. WL 0.011 CL 0.017 actual WL 0.010 CL 0.015

A-B: calc. WL 0.011 CL 0.017 actual WL 0.010 CL 0.015

Std. Dev.: within, S_w = 0.00395 between, S = 0.00410 S/S_w = 1.04

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					

R_1+R_2 calc. WL CL actual WL CL

R_1-R_2 calc. WL CL actual WL CL

Std. Dev.: within, S_w= between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	10	6	0	16
Std. Dev.:	0.003	0.002	-	0.003
Mean:	0.056	0.186	-	0.105
% RSD:	-			

Detection Criteria: 0.004

Test Name: POTASSIUM

Units: mg/L

Lab.: PR

Period: from 28/05/80 to 22/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: Samples are analyzed by AAS at 766.5 nm with an air-acetylene flame. Cesium, is introduced by an automated sampling train. Chart recorder results are converted to concentraion using manually prepared calibration curves.

Instrumentation: Technicon sampler; Gilson peristaltic pump; Varian AA275 (AAS); Linear recorder.

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
0.02 to 1.00	0 - 0.4 Abs.	0.01	6

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	21	0.60	0.603	0.003	0.0066
B	21	0.10	0.097	-0.003	0.0056
Long Term Blank:					
A+B	21	0.70	0.700	0.000	0.0107
A-B	21	0.50	0.506	0.006	0.0059

A+B: calc. WL 0.012 CL 0.018 actual WL 0.020 CL 0.030

A-B: calc. WL 0.012 CL 0.018 actual WL 0.020 CL 0.030

Std. Dev.: within, S_w = 0.0042 between, S = 0.0061 S/S_w = 1.47

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					

R_1+R_2 calc. WL CL actual WL CL

R_1-R_2 calc. WL CL actual WL CL

Std. Dev.: within, S_w= between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	16	3	2	21
Std. Dev.:	0.012	0.015	0.014	0.013
Mean:	0.079	0.340	0.635	0.169

% RSD: 1.9% Detection Criteria: 0.02

Test Name: SODIUM

Units: mg/L

Lab.: PR

Period: from 16/01/80 to 31/12/80

Sample Type: Precipitation

Sample Preparation:

Analytical Procedure: Samples are analyzed by AAS at 589.5 nm with an air-acetylene flame. Potassium is added with an automated sampling train. Chart recorder results are converted to concentration using manually prepared calibration curves.

Instrumentation: Technicon sampler; Gilson peristaltic pump; Varian AA-275 (AAS); Linear recorder.

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
0.01 to 1.00	0 - 0.5 Abs.	0.01	6

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	36	0.60	0.600	0.000	0.0061
B	37	0.10	0.098	-0.002	0.0055
Long Term Blank:					
A+B	36	0.70	0.699	-0.001	0.0083
A-B	36	0.50	0.502	0.002	0.0082

A+B: calc. WL 0.016 CL 0.025 actual WL 0.020 CL 0.030

A-B: calc. WL 0.016 CL 0.025 actual WL 0.020 CL 0.030

Std. Dev.: within, S_w = 0.0058 between, S = 0.0059 S/S_w = 1.01

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1					
R_2					
Digested Blanks:					
R_1+R_2					
R_1-R_2					

R_1+R_2 calc. WL CL actual WL CL

R_1-R_2 calc. WL CL actual WL CL

Std. Dev.: within, S_w = between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	29	9	1	39
Std. Dev.:	0.007	0.013	-	0.009
Mean:	0.071	0.286	0.700	0.137
% RSD: -		Detection Criteria:	0.011	

Test Name: AMMONIUM AND AMMONIA - LOW RANGE
Units: mg/L as N

Lab.: RL
Period: from 01/10/80 to 30/12/80

Sample Type: Rivers, Lakes, Precipitation

Sample Preparation: As per High Range

Analytical Procedure: As per High Range

Instrumentation: As per High Range but with a 5x expansion at the recorder.

Calibration:

Conc. Range	Operating Scale	Resolution	#Stds.
0.006 - 0.400	0 - 0.1 Abs.	0.004	2

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
C	92	0.300	0.3009	0.0009	0.00536
D	93	0.100	0.1062	0.0062	0.00364
Long Term Blank:	92	-	0.0082	-	0.0186
C+D	92	0.400	0.4072	0.0072	0.00740
C-D	92	0.200	0.1947	-0.0053	0.00543

C+D: calc. WL 0.011 CL 0.016 actual WL 0.008 CL 0.012
A-B: calc. WL 0.011 CL 0.016 actual WL 0.008 CL 0.012
Std. Dev.: within, S_w= 0.00384 between, S = 0.00459 S/S_w = 1.20

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R^1					
R^2					
Digested Blanks:					
R^1+R^2					
R^1-R^2					

R^1+R^2 calc. WL CL actual WL CL
R^1-R^2 calc. WL CL actual WL CL
Std. Dev.: within, S_w= between, S = S/S_w =

Duplicate Data:	0-20%	20-50%	50-100%	Overall
Number:	147	33	11	191
Std. Dev.:	0.004	0.006	0.009	0.005
Mean:	0.032	0.121	0.303	0.063
% RSD: 3%		Detection Criteria:	0.006	

Test Name: TOTAL PHOSPHORUS

Units: mg/L as P

Lab.: RL

Period: from 02/07/80 to 30/12/80

Sample Type: Rivers, Lakes

Sample Preparation:

Analytical Procedure: Samples are digested in a sulphuric acid-mercuric oxide-potassium sulphate media using two block digesters maintained at 200°C and 360°C. The pH is neutralized in line and the orthophosphate content in the digestate is determined by formation of a reduced phospho-antimonyl-molybdate complex using ascorbic acid as the reducing agent.

Instrumentation: Basic AA-II AutoAnalyzer plus two Technicon DB-40 block digesters. Std Cal(Std dev) = 4.16 (0.18)); 50 mm flow cells, 880 nm.

Calibration:

Conc. Range	Operating Scale	–	Resolution	#Stds.
0.003 to 0.200	0 - 0.36 Abs.		0.002	2

Quality Control Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
A	94	0.150	0.1518	0.0018	0.00129
B	94	0.050	0.0507	0.0007	0.00098
Long Term Blank:	93	-	0.0004	-	0.0008
A+B	94	0.200	0.2025	0.0025	0.00194
A-B	94	0.100	0.1011	0.0011	0.00123
A+B: calc. WL	0.002	CL 0.004	actual WL 0.004	CL 0.006	
A-B: calc. WL	0.002	CL 0.004	actual WL 0.004	CL 0.006	

Std. Dev.: within, S_w = 0.00087 between, S = 0.00115 S/S_w = 1.32

Recovery Data:

	Number of datums	Theoretical Concentration	Concentration Found	Ave. Bias	Std. Dev.
R_1	181	0.140	0.1409	0.0009	0.00457
R_2	178	0.084	0.0857	0.0017	0.00396
Digested Blanks:	83	-	0.0033	-	0.0035
R_1+R_2	91	0.224	0.2269	0.0029	0.00866
R_1-R_2	91	0.056	0.0552	-0.0008	0.00355
R_1+R_2 calc. WL	0.007	CL 0.011	actual WL	CL	
R_1-R_2 calc. WL	0.007	CL 0.011	actual WL	CL	

Std. Dev.: within, S_w = 0.00251 between, S = 0.00468 S/S_w = 1.87

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	266	50	12	328
Std. Dev.:	0.0020	0.0028	0.0038	0.0023
Mean:	0.017	0.066	0.142	0.029
% RSD: 2.5%		Detection Criteria: 0.003		

APPENDIX 2

Quality Control Data - Inorganic Contaminants Section

Test Name: LEAD

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	# Stds
G.F.AAS	217.0	.001-.200	0-0.60	.001	8
ICP		0-10			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	19	.0043	.0007	.0014	.0021	17%	.0038	114%
EPA 3/2	19	.056	.004	.008	.012	7.1%	.056	100%
ICP:								
MC-1	20	.0054	.0010	.0020	.0030	19%		
MC-2	22	.133	.0139	.028	.042	10%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	30	<.001	<.001
GFAAS:	10	.001	.001

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	74	2	4	80
Standard Dev.:	.0018	.005	.005	.002
Mean:	.0064	.028	.076	.010
% R.S.D.	28%	18%	7%	27%
Sample Conc. Range (µgm/ml)	0-.020	.020-.050	.050-.100	

Test Name: Copper

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	# Stds
G.F.AAS	324.7	.001-.200	0-0.90	.001	9
ICP		0-10			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	26	.003	.001	.002	.003	33%	.0037	81%
EPA 3/2	26	.019	.001	.002	.003	5.3%	.018	106%
ICP:								
MC-1	22	.0036	.0003	.0006	.0009	8.3%		
MC-2	22	.132	.0082	.016	.025	6.2%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	26	< .001	< .001
GFAAS:	10	.001	.001

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	69	4	2	75
Standard Dev.:	.00064	.00097	.0041	.00075
Mean:	.00245	.01685	.05785	.0047
% R.S.D.	26%	6%	7%	24%
Sample Conc. Range (µgm/ml)	0-.012	.012-.030	.030-.060	

Test Name: Iron

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	# Stds
G.F.AAS	248.3	.001-.200	0-0.90	.001	8
ICP		0-50			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	24	.011	.001	.002	.003	9.1%	.008	138%
EPA 3/2	24	.043	.003	.006	.009	7.0%	.039	110%
ICP:								
MC-1	22	.0185	.0011	.0022	.0033	6.0%		
MC-2	22	.183	.0065	.013	.020	3.1%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	26	.001	.001
GFAAS:	10	.003	.002

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	37	23	4	64
Standard Dev.:	.0052	.010	.0184	.008
Mean:	.022	.061	.157	.044
% R.S.D.	24%	16%	12%	20%
Sample Conc. Range (µgm/ml)	0-.040	.040-.100	.100-.200	

Test Name: Nickel

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	# Stds
G.F.AAS	232.0	.001-.200	0-0.50	.001	8
ICP		0-10			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	13	.0019	.0006	.0012	.0018	34%	.0016	120%
EPA 3/2	13	.047	.003	.006	.009	6.4%	.048	98%
ICP:								
MC-1	22	.0024	.0004	.0008	.0012	17%		
MC-2	22	.129	.006	.012	.018	4.7%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	28	<.001	<.001
GFAAS:	10	<.001	<.001

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	61	6	3	70
Standard Dev.:	.00031	.00134	.00084	.00042
Mean:	.00065	.0029	.0078	.0011
% R.S.D.	48%	46%	11%	46%
Sample Conc. Range (µgm/ml)	0-.002	.002-.005	.005-.010	

Test Name: Aluminum

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	# Stds
G.F.AAS	309.3	.005-.300	0-0.40	.001	7
ICP		0-50			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	27	.010	.003	.006	.009	30%	.0085	118%
EPA 3/2	27	.219	.029	.058	.087	13%	.218	100%
ICP:								
MC-1	22	.0168	.0039	.0078	.0117	23%		
MC-2	22	.222	.026	.052	.078	12%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	30	.002	.004
GFAAS:	10	<.005	<.005

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	37	28	5	70
Standard Dev.:	.0059	.012	.011	.0087
Mean:	.0233	.0568	.137	.045
% R.S.D.	25%	21%	8%	22%
Sample Conc. Range (µgm/ml)	0-.040	.040-.100	.100-.200	

Test Name: Zinc

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	#Stds
AAS	213.9	.002-.200	0-0.050	.001	2
ICP		0-10			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	8	.005	.002	.004	.006	40%	.0048	104
EPA 3/2	8	.013	.002	.004	.006	15%	.013	100
ICP:								
MC-1	22	.0240	.0015	.003	.0045	6.2%		
MC-2	22	.0514	.0026	.0052	.0078	5.1%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	28	<.002	<.002
GFAAS:	10	<.002	<.002

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	68	6	4	78
Standard Dev.:	.00105	.0035	.0069	.0015
Mean:	.0066	.0309	.0705	.012
% R.S.D.	16%	11%	10%	15%
Sample Conc. Range (µgm/ml)	0-.020	.020-.050	.050-.100	

Test Name: Manganese

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	# Stds
G.F.AAS	279.5	.001-.030	0-0.40	.001	5
ICP		0-10			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	26	.005	.001	.002	.003	20%	.0048	104%
EPA 3/2	26	.026	.002	.004	.006	7.7%	.024	108%
ICP:								
MC-1	22	.0036	.0002	.0004	.0006	5.6%		
MC-2	22	.109	.0058	.012	.017	5.3%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	30	<.001	<.001
GFAAS:	10	<.001	<.001

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	63	13	1	77
Standard Dev.	.0005	.0007	.0007	.00054
Mean:	.0039	.0117	.0468	.0056
% R.S.D.	13%	6%	1.5%	12%
Sample Conc. Range (µgm/ml)	0-.010	.010-.025	.025-.050	

Test Name: Vanadium

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	# Stds
G.F.AAS	318.4	.002-.300	0-0.30	.001	8
ICP		0-10			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	12	.009	.001	.002	.003	11%	.0085	106%
EPA 3/2	12	.223	.012	.024	.036	5.4%	.235	95%
ICP:								
MC-1	16	.00034	.00010	.0002	.0003	29%		
MC-2	22	.123	.0074	.015	.022	6.0%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	30	<.0002	<.0002
GFAAS:	10	<.002	<.002

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	64	4	3	71
Standard Dev.:	.0001	.00006	.0002	.0001
Mean:	.0003	.0011	.0036	.00048
% R.S.D.	33%	5%	6%	30%
Sample Conc. Range (µgm/ml	0-.0008	.0008-.0020	.0020-.0040	

Test Name: Cadmium

Units: µgm/ml.

Calibration:

	Wavelength nm.	Conc. Range	Operating Scale	Resolution	# Stds
G.F.AAS	228.8	.0001-0.020	0-0.50	.001	6
ICP		0-10			5

Quality Control Data:

	# of Datums	Mean	Std. Dev.	2X S.D.	3X S.D.	% R.S.D.	True Value	Mean % T.V.
GFAAS:								
EPA 2/100	23	.0006	.0001	.0002	.0003	17%	.00059	102%
EPA 3/2	23	.0118	.0018	.0036	.0054	15%	.014	84%
ICP:								
MC-1	22	.00038	.00004	.00008	.00012	11%		
MC-2	22	.0161	.0006	.0012	.0018	3.7%		

Blank Levels:

	# of Datums	Mean	Standard Deviation
ICP:	30	<.0001	<.0001
GFAAS:	10	<.0001	<.0001

Duplicate Data:

	0-20%	20-50%	50-100%	Overall
Number:	70	4	1	75
Standard Dev.:	.000085	.000073	.000035	.000084
Mean:	.000208	.00119	.00292	.00030
% R.S.D.	41%	6%	1%	39%
Sample Conc. Range (µgm/ml)	0-.0008	.0008-.0020	.0020-.0040	